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ALLOY SYSTEMS

PITMAN METALLURGY SERIES

ALLOY SYSTEMS

AN INTRODUCTORY TEXT

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To My Father

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Inspiring Teacher, Founder of the Department of Metallurgy
at The Ohio State University

Preface

This textbook is intended to be used in the teaching of metallography and physical metallurgy to college students. We sense the need for a text that bridges the gap between the elementary courses in physics and chemistry and the fundamental concepts of physical chemistry as applied to metals. These concepts include the phase rule and binary phase diagrams, thermochemical equilibrium, mass-action equations, and atomic structure of crystals. Most existing texts either assume previous acquaintance with these subjects or else brush them aside as being too advanced for an elementary text on the behavior of alloys.

The author feels that such subjects are not too advanced if sufficient time be given to their clear exposition. It should be no more difficult to develop physicochemical concepts as applied to metals and alloy systems than to develop them for chemical systems, generally; and it should be easier thereby to capture interest.

However, the principles underlying these concepts should be understood thoroughly and precisely. The phase-equilibrium diagram is heavily laden with information for him who can interpret it; but it can be, and often is, badly misinterpreted by the novice who is improperly instructed as to its true meaning. For this reason, the first part of the book is given to a rather detailed discussion of different types of binary equilibrium diagrams with precise instructions for their interpretation. It is urged that students be required to understand and memorize rules and definitions regarding these diagrams, and that they check their deductions against these rules.

The writing of the book was started as a series of lectures designed so that, with the aid of mimeographed abstracts, the average student could assimilate the lecture on hearing it once. This origin accounts for the rather loose or open style. The attempt has been made to maintain this style throughout the book and to keep the book readable.

Yet the approach to the subject is not essentially different from the conventional one in books on physical metallurgy, except as the attempt has been made to emphasize the educational aspect. The theory of phase equilibria is developed as the logical consequence of a few simple postulates regarding the relationship of freezing characteris-

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tics to composition, and finally arrives at what might be considered a
practical confirmation of the phase rule. The purpose of this proce-
dure is to stimulate the student's thinking and imagination in regard
to the structural variations that might be encountered in the alloy
systems, and to deter him from accepting categorically the results of
the phase rule without full understanding of their physical signifi-
cance. After this has been accomplished, the phase rule itself is dis-
cussed, and immediately confirms all previous deductions.

A chapter on "Deviations from Equilibrium" is introduced, to em-
phasize the fact that true equilibrium does not exist, but merely repre-
sents the ideal condition toward which alloy systems tend to revert.
In this chapter the phase relationships of nonequilibrium alloys are
shown, after the method of Giolitti, in relation to the true equilibrium
diagram, and the mechanism of solidification under nonequilibrium
conditions is discussed.

Selected commercial alloy systems are dwelt upon at length with
two purposes in view. The first is to apply and expand the student's
newly acquired knowledge of phase-rule chemistry; the second is to
give him a useful, practical introduction into the technology of each
alloy system undertaken. For this latter purpose it was felt necessary
to devote some space to the process metallurgy of the parent metals
involved. Actually, the physical metallurgy and metallography of
commercial alloys are intimately interwoven with characteristics and
defects that have their origin in the smelting and processing opera-
tions.

The space given to the manufacture of iron and steel (Chapter XI)
and to defects and impurities in steel (Chapter XII) may seem super-
fluous for some curricula where these subjects are covered in sep-
arate courses. The same may be said of the chapter on physical and
mechanical properties (Chapter XV); and yet it is felt that the inclu-
sion of these chapters will increase the usefulness of the text to groups
who would otherwise have no acquaintance with those phases of
metallurgy.

Since this book is primarily a textbook, the addition of questions
and problems to supplement each chapter seems obligatory. However,
it will be realized that the mode of presentation, as the logical devel-
opment of a thesis, does not always lend itself easily to simple ques-
tions and answers. Particularly in the early chapters, the conclusions
of the text are so pointed that questions regarding them seem trivial.
Of course the problems on crystal structure, the lever reaction, and
the phase rule are highly justified as a means of fixing these concepts
in the student's mind; but pointed questions on the descriptive mat-

ter are so easily answered by thumbing back a few pages that they hardly seem worth while.

Again, it is realized that the character of the subject involves much information and material that must be omitted from a book of this size. Such material may well embellish the instructor's lectures and constitute subject matter for outside reading on the part of the student. To stimulate such interest and activity, questions touching this extraneous subject matter seem more highly justified than questions answered specifically in the text.

In the first fourteen chapters the questions to which answers should be found in the text are listed under one heading while those requiring information from other sources are listed under the heading, *Supplementary Questions*. Problems are also listed under separate headings in these chapters.

In the latter part of the book, the two types of questions and the problems are not separated, inasmuch as most of them require information or skill not supplied directly by the text.

No attempt is made to cover all alloys or alloy systems. The systems selected, namely those based on iron, copper, aluminum, and magnesium, comprise the most useful and popular alloys known and should illustrate enough basic principles to start the student well on his way in the field of metal technology. Bearing metals, complex hard alloys and tool materials, powdered-metal compacts, and many other subjects of physico-metallurgical importance are consciously omitted in the realization that the book must have an end.

The mature reader will recognize in much of the text the influence of the late Dr. Albert Sauveur. Although the author was never a student in Sauveur's classes, his first introduction to metallography was through Sauveur's original book, *The Metallography and Heat Treatment of Iron and Steel,* a book that stands out as one of the finest of textbooks. Much of the author's viewpoint with regard to the interpretation of equilibrium diagrams and phase chemistry has been derived from the teachings of Dr. W. J. McCaughey, Professor of Mineralogy at Ohio State University. Frequent use has been made of the help and advice of the author's colleagues, Professor D. J. Demorest and Professor William A. Mueller, both of the Department of Metallurgy at Ohio State University. Professor Demorest and Professor Mueller have supplied particularly helpful suggestions in the fields of ferrous process metallurgy and nonferrous process metallurgy respectively.

The author also acknowledges with thanks the help of Mr. Frank T. Sisco, Metallurgist and Editorial Director, Alloys of Iron Research,

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ALLOY SYSTEMS

CHAPTER I

The Metallic State Defined

The Defining of Metals · Metallic Characteristics and Properties · Alloys · Amphoteric Elements · The Use of the Microscope in the Study of Metals · Additional Physical Tests

The earliest human acquaintance with metals probably came about through the finding of gold or copper nuggets since these have the two metallic characteristics that would be most likely to attract the primitive savage in his wanderings, namely, the bright luster and the malleability. These two characteristics would distinguish the metallic substances from all others with which he would be likely to come in contact. Similarly, in our own childhood experiences, our attention was attracted by spectacle rims, a gold watchcase and chain, the silverware on the table, and safety pins and hair pins that could be readily bent out of shape by small hands.

As civilization progressed more kinds of metals were discovered and it was found that they could be put to many uses other than decorative. They could be easily formed into a variety of shapes. They had strength and reliability, and would not break with rough handling. It was also found that all metals did not occur naturally in the native or metallic state, but that many of them occurred as kinds of rock or earthy materials from which they could be reduced by fire and carbon, and it was found that many of these tended to revert to the earthy form upon exposure to air and moisture for long periods of time.

With the advent of electrical knowledge metals acquired a special importance because of their ability to transmit electric current.

The Defining of Metals

Efforts to define the term metal have led to some confusion. This is, in part, due to differences in the scope and purposes of the definitions

and, in part, to ambiguity regarding the classification (i.e., metal or non-metal) in which certain substances should be placed. Much confusion in definitions arises from a misunderstanding of the purpose of the definition. Scientific definitions may be informative or categorical, but it is frequently impossible to devise a definition that is both informative and categorical. The informative definition seeks merely to acquaint the reader or listener with the subject at hand, precise limitations and details to be relegated to further study. The categorical definition, on the other hand, is for the purpose of isolating its subject to the exclusion of all possible misinterpretation, regardless of how complex such a process may be.

For example, a number of years ago textbooks in chemistry defined metals as substances which formed electropositive ions in solutions of their salts. Such a definition, although perfectly unintelligible to a novice, dwelt upon a property of metals that could be definitely ascertained and left no room for infringement by other types of substances. It enabled the chemist to classify his elements perfectly, regardless of whether that classification agreed with previous conventional classifications or popular conception.

However, from the engineering standpoint, we must recognize convention and define our metals, first, to inform the novice, and secondly, to include substances which are popularly classed as metals.

As we look over the periodic table we are surprised to find that about 66 elements are considered definitely to be metals, 14 are definitely non-metals, and 9 are in a somewhat doubtful category.[1] At first thought it might seem odd that with such an array of metals they should attract attention, but it must be remembered that only rarely do metals occur uncombined with non-metals, and also, as regards the quantity in the earth's crust, oxygen alone, a non-metal, composes almost 50% of all the solid and liquid material; silicon, one of the doubtful elements, makes up more than half of the remainder; and aluminum, iron, and calcium, in combined form, make up most of what is left. And yet, quite apart from any chemical or scientific considerations, the doctor, the lawyer, the tradesman, the politician, and we ourselves all seem pretty confident that we know a metal when we see one. Consider a list of substances such as clay, iron, tin, soap, rubber, brass, coal. Any normal person over eight years of age should be able to pick out the metals without hesitation. Why worry then about electropositive ions when formulating a definition? It should be pos-

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[1] It is not intended in this rough classification to place all the elements in the periodic table. The transuranian elements and the extremely rare elements are not under consideration.

sible to base a sound definition on those characteristics with which we are all acquainted. And here let us note that we shall consider metals, not from the chemical standpoint as elementary substances, but rather from the layman's standpoint as any substances that exhibit those characteristics which we term metallic. That is, we shall consider what is known as the metallic state.

Metallic Characteristics and Properties

Probably the first thing that attracted the savage or the child was the fact that metals were bright and shiny. Let us chalk up that characteristic as (1) *metallic luster.* All metals have it, and the most highly developed scientific research has not changed our ideas on that point. We find upon investigation, however, that the peculiar type of luster that metals have is due to a combination of two things, a rather highly reflecting surface and a high degree of another characteristic (2) *opacity.* All metals are opaque although some of the noble metals can be beaten into thin enough sheets to transmit a small amount of light.

Probably the next important characteristics that distinguish metallic substances from most others derive from their ability to be permanently deformed without breaking. Depending upon the method of deformation, these characteristics are known as (3) *malleability* and (4) *ductility.*

A very little experience in the use of metals teaches us that they conduct heat readily. We call this property (5) *thermal conductivity.* More scientific ideas that the child or the savage might not be expected to know lead us to include (6) *electrical conductivity,* (7) *thermoelectric* effects, and, with due regard for the chemists, (8) the formation of *electropositive ions* in solution.

As we scan this list of characteristics and properties, we can think of many metals that do not have all of them; none, however, is without the first, namely, luster. On the other hand, we know of some non-metallic substances that have luster similar to metals—pyrite, for instance—and others with some of the properties in varying degree. Graphite is a fair electrical conductor, waxes are malleable, and periclase (MgO) and silicon carbide (SiC) are fair conductors of heat. A satisfactory definition then would list the above properties and characteristics and state that a metal was a substance that had *most* of them, including luster.

Alloys

So far we have considered the metallic state generally. Specifically, we must distinguish between metals and alloys. The distinction is,

however, very simple. Alloys are merely solid mixtures of metals that serve useful purposes. It does not matter how the mixture is effected, or whether the metals are mutually soluble, or whether they can be separated into two or more liquids when melted, like oil and water. So long as the mixture forms a solid mass that serves a useful purpose it can be called an alloy. Sometimes non-metals are included in the mixture, for example, carbon in iron, but as long as the mixture exhibits metallic characteristics it is still an alloy.

Amphoteric Elements

Of course, since our classification seeks to divide all elementary substances into two categories of metal and non-metal, we shall find borderline cases that may fit both categories, but imperfectly. These are the so-called amphoteric elements, examples of which are arsenic, antimony, silicon, selenium. Other elements are metallic under certain conditions and non-metallic under others. Such a substance is tin, which changes at low temperatures to a powdery form that in no way resembles the form in which we ordinarily see it. Discussion of the ultimate criteria for such substances is a subject for more advanced treatises and belongs in the field of atomic physics.

Use of the Microscope in the Study of Metals

The *science of metallography* deals with the structures of metals and alloys. That metals and alloys have structures is readily shown by means of the microscope; so the microscope is the principal tool used in the study of metallography.

Since metals are opaque substances, it is not possible to pass light through them for microscopic study, as is done in medical, biological, and mineralogical work, but instead, they must be viewed by light reflected from the surface of the specimen. The particular surface examined will be expected to reveal the internal structure of the specimen, so this surface must be prepared by cutting through the piece with a saw. The newly sawed surface will be studied after all saw marks and scratches have been carefully polished away. The technique of preparing such a surface in a piece of metal makes a simple and not unduly tedious laboratory exercise.

After the surface is thus prepared it is like a mirror and is without features, except for non-metallic inclusions and voids. In order to show the metal structure it must be thrown into slight relief by etching in dilute acid or some appropriate solvent.

The next step is to view this surface by reflected light and magnified under the microscope. The microscope and illuminating outfit are

arranged so that the light falls vertically on the surface of the specimen from which it is reflected to the lens of the microscope. This is accomplished by a small mirror or prism in the tube of the microscope. The light is now brought to this mirror through the side of the tube and reflected downward through the objective lens by which it is focused on the specimen. The advantage of this method is that it produces a brilliantly illuminated specimen and shows the structural features as an easily interpreted pattern.

Additional Physical Tests

The microscope, however, is not the only tool used in metallography. Probably the most important thing to know about any piece of metal or alloy is its chemical composition, for without that we cannot be sure that we know even what kind of metal it is. Any physical test that will

Figure 1.1. Path of light through metallurgical microscope.

add to our general knowledge of the metal will be of use in determining and interpreting its structure. Tests of strength, ductility, thermal and electrical conductivity, specific heat, and volume are all used. Of special importance are x rays in studying metals.

QUESTIONS ON THE TEXT

1. What is the commonest metallic atom in the earth's crust?
2. What single characteristic is common to all metals?
3. What are amphoteric elements? Name four.
4. How does the metallurgical microscope differ from most others?
5. Are hardness and strength essential metallic characteristics?

SUPPLEMENTARY QUESTIONS

To answer these questions requires knowledge or reading outside the text.

1. Show how the metallic bonding by the so-called "free" electrons can account for all the metallic characteristics.

2. What metallic characteristics do each of the following substances possess: copper; antimony; quench-hardened steel; indelible pencil; graphite?

3. What are electropositive ions?

4. Name 10 common nonmetallic elements.

The Crystalline Nature of Metals

Crystalline Substances · Evidence that Metals Are Crystalline · Bragg's Law and Its Application · Crystal Analysis and Space Lattices

Crystalline Substances

As we study metals and alloys we soon discover that they are crystalline substances. A crystalline substance, as we shall use the term, is one made up of crystals or parts of crystals, so that, in these parts, the smallest units of structure, i.e., the atoms or molecules, are conceived to be arranged in an orderly or regular geometric pattern in space. The external form of the crystal or part of a crystal does not matter as long as its internal molecular structure is crystalline.

Evidence that Metals Are Crystalline

We may enumerate some of the kinds of evidence that metals are crystalline.

Geometric Forms

In the shrinkage cavities of large masses of metal which have solidified after being melted and cast, notably ingots, we sometimes find portions of metals of very apparent external crystalline form. If the shrinkage cavity is deep, as in steel ingots, we may occasionally obtain large beautiful specimens weighing several pounds. (Figure 2.1.) On the other hand, with very slight shrinkage on solidification, the crystalline structure may be shown as a pattern on the top surface.

Etching Pits

Probably the first conclusive proof that all metals are crystalline lies in the existence of what are known as etching pits on speci-

mens that have been prepared for microscopic examination. To secure a clear understanding of these it will be necessary to consider the microstructure of pure metals. With the specimens prepared as described, truly pure metals, in the cast or annealed condition, all exhibit practically the same design under the microscope. The surface is made up of light-colored polygonal areas bounded and separated from each other by fine dark lines. Carried into three dimensions this structure indicates grains of uniform material that are packed together in a non-porous aggregate. These grains have approximately the same dimensions in any direction, a condition known as equi-axed. They are called polyhedral grains, which means *grains with many faces.* The pattern that we see on the two-dimensional sections through the structure is due to the fact that the material at or near the grain boundaries dissolves much more rapidly in the etching solution than the material

FIGURE 2.1.   Photograph of iron dendrite.

in the interior of the grains. Thus the grain boundaries appear as dark narrow trenches surrounding and separating the grains. (Figure 2.2.)

Now if the etching is allowed to proceed for a longer time, the interiors of the grains are attacked, and often in a peculiar fashion. Small pits are formed. Close examination shows that these are not just round cavities but have polygonal outlines, usually triangular or quadrilateral. The most interesting thing about them is that when several such pits are found in one grain, it is found that their sides are parallel. Between the pits in different grains, however, no such relationship exists. (Figure 2.3.)

The only explanation of this variation and relationship of pits is that each grain has a definite crystalline structure and orientation. A characteristic of crystals is that they precipitate or dissolve at different

rates in different directions. The first is commonly known, but the second is no less true. Hence, when the acid or etching solution begins to attack the material at points other than grain boundaries it produces a pit whose shape betrays the crystalline nature of the metal. This can be shown for all metals.

Microstructural Patterns

Alloys of metals sometimes have two or more kinds of crystals in them. The first of them to form, when the alloy freezes, crystallizes freely and is then surrounded by the other material. The reg-ular crystalline outline of the first material is then clearly evident in the microsection.
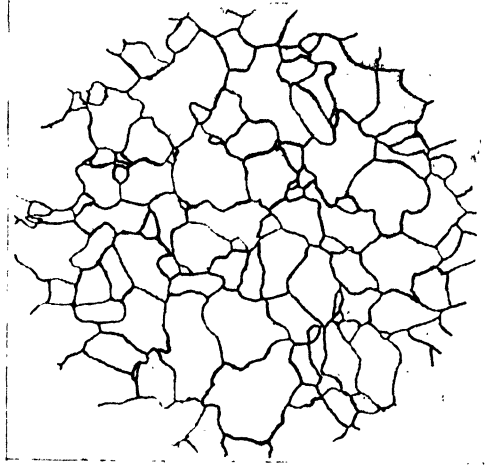
FIGURE 2.2. Microstructure of a pure metal.

FIGURE 2.3. Etching pits in copper, 500×.

Latent Heat

A characteristic of pure substances that crystallize when they freeze is that latent heat is produced during freezing so that there is a delay in the drop in temperature while freezing takes place. This is observed for all metals.

Bragg's Law and Its Application

X-ray Diffraction

The final and uncontrovertible proof that metals are crystalline is by means of x rays. The x-ray diffraction pattern is obtained only with crystalline substances, and all metals give it. To understand this we shall develop the law of diffraction by reflection from plane surfaces. The application of this law to the scattering of x rays by crystals was suggested by W. H. and W. L. Bragg, and it is sometimes referred to as Bragg's law.

Like light, x rays are wave phenomena. We are acquainted with some of the results of this fact in the behavior of light, particularly in that class of phenomena known as interference. Interference is best understood by considering two trains of waves traversing the same path. Several cases may arise:

1. If the crests of one train of waves are in such a position as to be just superimposed on the crests of the other, the result will be a beam of double intensity.

2. If the crests of one train fall exactly between the crests of the other, there will be extinction of the beam.

3. All other relationships will result in light of less intensity than that of the first case.

These conditions can be realized by allowing a beam of light to fall on parallel surfaces of glass that are very close together. The resulting beam will be made up of light reflected from both surfaces, and for light of one certain wavelength (waves of one particular frequency) the first condition will be fulfilled, whereas for all other wavelengths the other two conditions obtain. The color, therefore, represented by one wavelength, will be intensified, while all other colors will be suppressed. The particular wavelength that is intensified can be varied by varying the reflecting angle, which causes a small variation in the relative distances the two reflected beams must travel. This is the explanation of the well-known phenomenon of Newton's rings, in which, by pressing two clean plates of glass together at a point, we observe rainbow-colored rings around the point by reflected light. It is also commonly observed, in crude form, as an iridescent appearance in cracks in ice or glass.

The only other condition necessary for interference to occur is that the distance between the reflecting surfaces must be of the same order of magnitude as the wavelength of the light.

In searching for a measure of the wavelength of x rays, Dr. Max von Laue considered the feasibility of using the layers of atoms in a crystalline substance as reflecting surfaces, and calculating the wavelength by the laws of interference and the intensification angle for a beam of monochromatic x rays. This method worked out very well, using crystalline substances in which the distance between planes of atoms had been determined by physicochemical means. However, it also offered a simple and relatively easy method of determining distances between planes of atoms in crystals of all kinds.

The laws involved are easily demonstrated. Consider certain planes of atoms in a crystal exposed to a beam of x rays. The train of waves $A'B'C$ travels the same path from B to C as the train ABC. The difference in length of path, however, is the difference between AB and $A'B'B$. If we extend $A'B'$ to D then $B'D = B'B$. Now drop a perpendicular from B to N on $B'D$. Then $AB = A'N$ so that the difference in path is $B'D - B'N = ND$. But $ND = 2d \sin \theta$. Now if this differ-
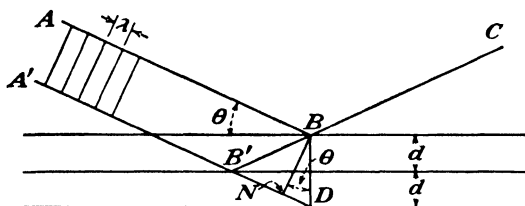
FIGURE 2.4. Illustrating Bragg's law.

ence in path is a whole number times the wavelength λ, condition one will be fulfilled and the beam BC will be intensified. Therefore the formula

$$n\lambda = 2d \sin \theta$$

is derived where n is a small whole number.

This law gives the relationship between wavelength, angle of incidence, and distance between planes of atoms. Usually n equals 1 and is easily found, so that if x rays of known constant wavelength are used, θ becomes a measure of d. However, θ must be found by trial, and several methods are used. The location of the intensified beam must be found by its action on a photographic plate or film. In one method a single crystal, while exposed to a narrow beam of x rays, is rotated slowly through every possible angle. Whenever the angle

happens to be correct the position of the diffracted beam is registered on the plate.

The simplest method for metals is to use a piece or wire of the metal,
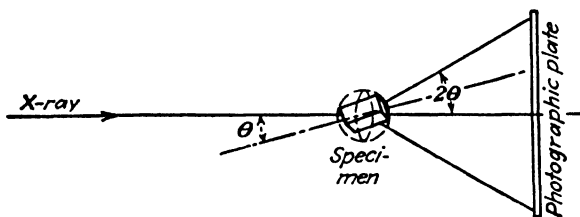
FIGURE 2.5.   Rotating-crystal method for finding θ.
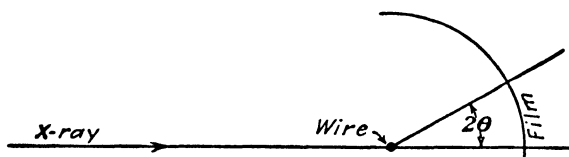
FIGURE 2.6.   Fine-powder or wire method for finding θ.

which is made up of fine crystals. If the crystals are sufficiently fine there will always be some turned at the correct angle. This is the same as the fine-powder method for brittle materials.

The setup shown results in a plate with a set of concentric rings whose radii are a measure of the angle θ. It is not necessary to show the whole ring, however, and for accuracy and simplicity the film is arranged on the arc of a circle about the specimen, as shown in Figure 2.6.

Crystal Analysis and Space Lattices

Of course in a crystal we can trace several different sets of planes of atoms. Some sets are quite similar, like the side, top, and front of a cube, and will give the same value for d and θ.
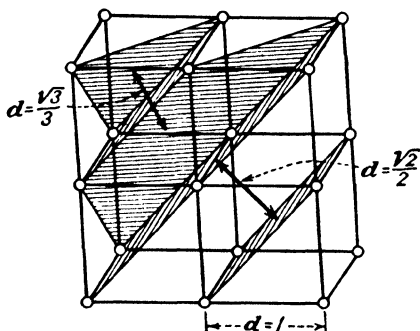
FIGURE 2.7.   Spacings in simple cubic lattice.

Other sets of planes will be at specific angles to each other and will give different values for d and θ. We can see this in the simple cubic lattice shown in Figure 2.7.

We will obtain, therefore, a series of lines on the photographic film, each representing a set of planes of one spacing or value for *d*. It is then the job for the crystal analyst to find out what kind of crystal will give rise to the particular set of spacings. This is sometimes tedious but not so difficult as might be imagined, particularly for metals, nearly all of which fall into one of three classes.
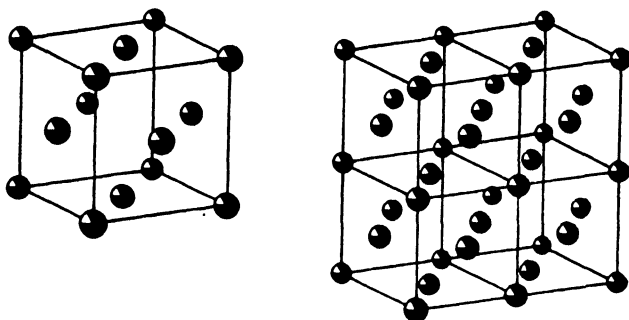
FIGURE 2.8. Face-centered cubic lattice; single cube and four cubes.
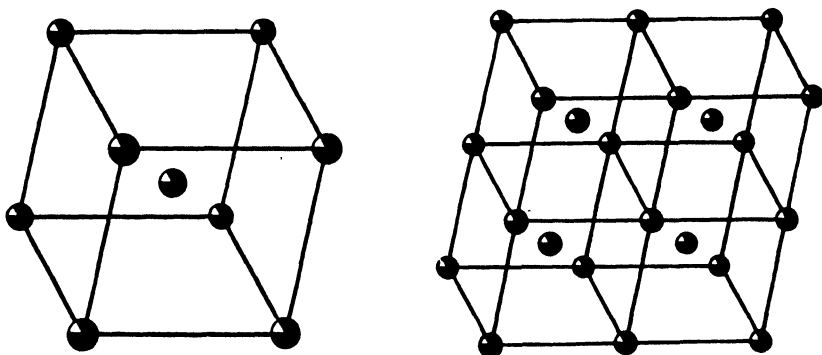
FIGURE 2.9. Body-centered cubic lattice; single cube and four cubes.

One of these classes is the face-centered cubic lattice. In this the atoms are arranged as shown in Figure 2.8. They are considered to be at the corners of cubes with an atom at the center of each cube face. Such a configuration is called a space lattice and, geometrically, space lattices are merely convenient methods of describing the various possible symmetrical arrangements of points in space. The face-centered cubic lattice might also be considered to represent the positions of the centers of balls of equal size when they are packed together in the closest possible manner.

The lattice in Figure 2.8 is highly symmetrical and, as a matter of

fact, we can consider any atom as a cube corner or as a face atom and trace the structure equally well among the other atoms.

Another common lattice for metals is the body-centered cubic lattice. This has an atom at the center of each cube, instead of the faces. Here, again, each atom is just like every other atom and can be considered as a corner or center atom.

The third type, known as the close-packed hexagonal lattice, will be discussed in Chapter XXVIII.

When you solve the questions and problems below you should find that the symmetry of the face-centered cubic lattice is greater than that of the body-centered cubic. Plastic flow in metals—ductility or malleability—is in part dependent upon this symmetry, and we find that all those metals which crystallize in the face-centered cubic system are very soft and malleable. Examples are lead, gold, silver, copper, nickel. The body-centered cubic metals, on the other hand, are much less soft, some being quite hard and even brittle, for example, iron, chromium, tungsten, molybdenum.

Many characteristics of metals are traceable to the nature of the space lattice, and we shall have occasion frequently to mention it. As regards the evidence of crystallinity, the x ray shows diffraction lines only on crystalline substances. We are assured, therefore, of the definitely crystalline nature of metals.

QUESTIONS ON THE TEXT

1. Define a crystalline substance.
2. How do etching pits indicate that metals are crystalline substances?
3. What is meant by light interference?
4. What is actually determined about the crystal lattice by use of the x ray and Bragg's law?

PROBLEMS

1. How will an increase in d affect the value for θ and how will θ be affected if n is 2 instead of 1?
2. Assuming that the side of a single cube in the face-centered cubic lattice equals 1, what is the distance between closest atoms?
3. How many closest neighbors has each atom in the face-centered cubic structure?
4. What is the ratio of atoms to cubes in the face-centered cubic lattice as a whole?
5. If the side of a single cube equals 1 in the body-centered cubic lattice, what is the distance between closest atoms?
6. How many closest neighbors has each atom in the body-centered cubic system?

7. What is the ratio of atoms to cubes in the body-centered cubic space lattice?

8. Any atom in the face-centered cubic system or in the body-centered cubic system can act as a corner atom upon which can be constructed a system of cubes similar to the original system and with faces and edges parallel to those of the original system. How many such systems are in the face-centered cubic lattice? In the body-centered cubic lattice?

CHAPTER III

How Conditions of Solidification Affect Metal Structure

Persistence of Crystallinity · The Behavior of Stressed Crystals— Slip Lines · Formation and Growth of Crystals—Dendrites · Cooling of Metals from the Molten State · Freezing and the Cooling Curve · Constant Freezing Temperature · Cooling Curves and Composition · The Binary Equilibrium Diagram

We have seen that metals are crystalline substances; that they are crystalline in the sense that the atoms of which they are composed are arranged in a definite geometric pattern or space lattice; the microscopic examination shows the metal to be made up of equi-axed, polyhedral grains and that these grains have internal crystalline structure as indicated by etching pits, although their external shapes are not those of crystals.

Persistence of Crystallinity

It is very important that we realize that metals are crystalline, as we study metal structures, because we shall find that the mechanism of crystal formation and crystal growth is a controlling factor in the development of these structures. Furthermore, we must realize that solid metals are very persistently crystalline and, no matter what we do to them, they continue to be so. No amount of mechanical working, for instance, can destroy this characteristic. To be sure we may crush the grains, but this merely results in smaller and more numerous ones; all still crystalline.

Behavior of Stressed Crystals—Slip Lines

Let us think for the moment about what happens to the crystals of a piece of metal when it yields to a stress, without actual fracture but

undergoing that peculiar type of strain known as plastic deformation. Imagine a cube of copper, polished and etched on one side to show the crystal grain structure. Suppose we arrange a microscope so as to be able to observe the polished side of the cube while it is being squeezed out of shape by some machine designed for the purpose.
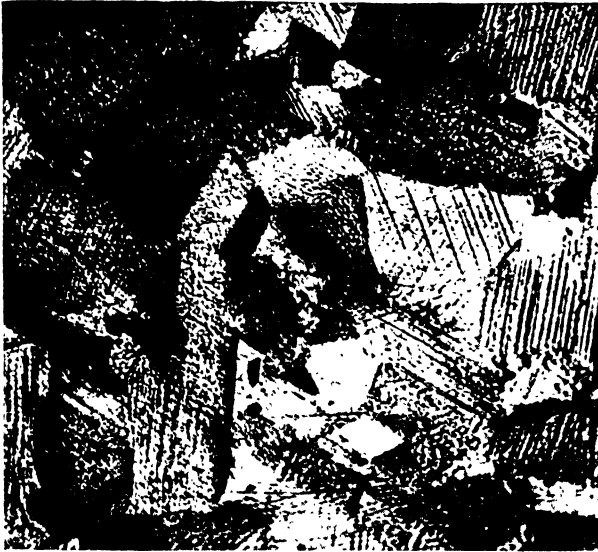
FIGURE 3.1.   Slip lines in a face-centered cubic metal (copper), 200×.

Now if we observe it while it is being squeezed, we will witness an interesting series of changes. Up to the time when the *elastic limit* is reached the polygonal grain boundaries will undergo no change, but shortly after this, we shall see groups of fine parallel lines appearing in many of the grains. The lines in any one grain will be parallel, but there will be no relation between the lines in different grains (Figure 3.1). As the squeezing continues, the lines will become more numerous and new sets of parallel lines will appear in each grain which are not parallel to the first set. The grains will become flattened, finally, in the direction of the stress and the lines so numerous that they do not show up individually but merely give the grain a roughened appearance. Still further stress increases the flatness of the grains and mussiness of their surfaces until the grain boundaries themselves become indistinguishable, and the whole specimen assumes a fine indefinite structure.

It has been definitely proved that the directions of the parallel lines, first observed, are the same as the direction of planes of atoms in the

crystal. These lines are called slip lines and are the traces of planes in the crystal called slip planes. They have a counterpart in the cleavage planes of certain minerals, such as calcite and mica, but are different in that, instead of being planes of weakness, they are planes along which flow or sliding may take place without rupture. This manner of flowing or sliding in metal crystals is termed slip. The requirements for slip are that the crystal have a high degree of symmetry, which most metals have, and that the atoms of the metal be all, or nearly all, alike so that in sliding past one another no new crystallographic or chemical relationships are involved.

Thus we see that flow can take place in a metal crystal without the crystal structure being destroyed, at least, not in the main body of the crystal. We are faced with a dilemma, however, when we consider more than one crystal subjected to plastic deformation. How can slip be transmitted across the boundary between two adjacent crystals of different orientation, or perhaps several boundaries of several crystals? It would seem as if fracture would have to occur in some of the crystals. The only solution seems to be in assuming a greater degree of mobility and plasticity in the grain boundaries than in the grains themselves, so that the overlap and maladjustment between different crystal directions in different grains can be absorbed in a sort of fluid, albeit highly viscous, grain boundary.

This idea of a fluid, or amorphous grain boundary has been the subject of much discussion among metallurgists. It was first proposed by an Englishman named Beilby,[1] who unfortunately incorporated some untenable hypotheses regarding its nature. Some have found occasion to discredit his theory, and even ridicule it. In all probability it is not strictly correct and would have to be modified to afford an exact picture of the conditions existing at grain boundaries. However, if we assume that for a very small space in the vicinity of the boundary between grains of metal, the structure is not crystalline, but that of a highly viscous liquid[2] even at ordinary temperatures, we can explain many puzzling characteristics of metals.

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[1] "The Hard and Soft States in Metals," by George T. Beilby, *J. Inst. Metals*, 6:2, 5–43 (1911).

[2] Glass is considered to be a highly viscous liquid. A characteristic of such substances is that they flow at high temperatures and under slowly applied loads but fracture in a brittle manner under rapidly applied loads or low temperatures. As is pointed out by Dr. Zay Jeffries and R. S. Archer in their book *The Science of Metals* (McGraw-Hill Book Co.), this behavior fits metals very well. At low temperatures or under rapidly applied loads, metal fractures are independent of grain boundaries whereas at high temperatures or under slowly applied loads, the grains pull apart, indicating that the grain boundary is weak and plastic.

Formation and Growth of Crystals—Dendrites

This brings us to the most important consideration regarding the metal structures, namely, how they are formed. To most of us the existence of a crystal or crystalline substance implies a process of crystallization that has taken place some time. So it is with metals. Usually, the crystallization has taken place as the result of solidification from the molten condition, although, as we shall see, crystallization can take place in solid metal that is not molten. (*Note:* This is not in any way connected with the so-called crystallization of metals that break for no apparent reason under dynamic stresses, e.g., automobile axles. Such is not crystallization at all, but a form of what is known as fatigue, which will be discussed in Chapter XV. True crystallization in metals is a healing process that relieves strains.)

The manner in which metals crystallize on solidification from the molten state is peculiar and not usually evident from the microstructure. Consider a mass of molten metal that has been cast into a mold. As the temperature of the metal is lowered by loss of heat through the sides of the mold, a time arrives when freezing commences. This will be indicated by the formation of solid metal around the sides of the mold. Now if we could watch the process through a microscope, and if the metal were transparent so that we could see what went on underneath the surface, we would see a very remarkable and beautiful sight. Starting at the surface of the mold, little needles of solid metal would form and develop, by lengthening, into the liquid metal. At frequent intervals new needles would form on the sides of these first needles and develop in a direction at right angles to them. Then more needles would form on the sides of these needles and develop in a direction at right angles to

FIGURE 3.2. Growth of a dendrite.

them. Then more needles would develop on the second set, and so on until the whole mass was practically filled with the branching structure. If, before the whole mass is solid, we could remove the solid portions from the liquid, we would find that they somewhat resembled

little pine trees in that they have a main branch developing into a multiple system of side shoots. The structure of any one system, would, however, be much more regular than a pine tree and the branches would be developed at exactly right angles to each other.

As solidification of the metal in the mold becomes complete, the growth of branches to our tree finally fills up all the available space
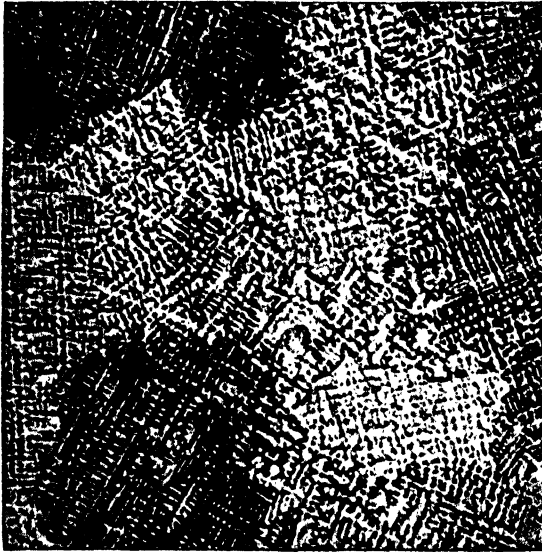
FIGURE 3.3. Dendritic character of crystal grains in a gold alloy, 100×.

and uses up all the liquid. If we started with a perfectly pure metal and, after it had solidified, made a microsection, properly polished and etched, all evidence of the branch structure will have disappeared because the branches have all closed together in a solid mass and there is no way to distinguish them. If, however, we had started with an impure metal, or an alloy, where selective crystallization occurred, or the composition of the liquid had changed during solidification, the traces of the branches might be, and often are, quite clearly evident in the microsection. (Figure 3.3.)

These branching structures are called dendrites, the word *dendrite* meaning a bushlike structure. They are really metal crystals and grow as a result of crystallization from the melt. Similar crystal growths are commonly observed in snow and frost. This type of crystallization is known as dendritic crystallization and is characteristic of most metals.

Now when two dendrites of independent origin grow side by side, or adjacent to each other, they will not, in general, be turned so that

they can join together as a single crystal. Instead, as they use up and share all available liquid between them, they will meet along a boundary surface that bears no relation to the crystallographic directions of either dendrite. Often the boundary will be quite irregular and crooked, or warped. Thus we account for the polyhedral grains seen under the microscope when we observe the section of a solid piece of pure metal.

Since most metals and alloys that are in commercial use have to be melted at some stage of their manufacture or fabrication, and since many metals acquire special properties as the result of systematic heatings and coolings through certain temperature ranges, a process known as heat treating, there is ample justification for an extended study of the thermal characteristics of metals and alloys. Knowledge of their melting and freezing temperatures and their specific heats adds tremendously to our knowledge and understanding of structures. In fact, thermal characteristics and metal structures are very intimately connected and interdependent, as we shall soon discover.

Cooling of Metals from the Molten State

The thermal characteristics that we study first may be, quite naturally, the freezing temperatures. These are most simply determined by making time-temperature cooling curves for the metals in question. This determination is easily accomplished by melting a crucible full of the metal and allowing it to cool while temperature measurements are made of it at uniform time intervals. The time intervals are plotted on coordinate paper as abscissas, the temperatures as ordinates. The temperatures may be determined by the thermoelectric method,[3] and it may be well to review this method, briefly, for the benefit of those who are not acquainted with, or have forgotten it.

By the Seebeck effect, well-known in elementary physics, when a junction of two dissimilar metal wires is heated, an electromotive force is produced between the cold ends of the wires, and a current will be registered if these cold ends are connected through a galvanometer. The emf produced, or the current generated, will be dependent on, and roughly proportional to, the difference in temperatures between the hot junction and the cold ends. Properly calibrated

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[3] The method described here is only one of several. For metals of very high melting temperature, optical or radiation pyrometry is used. Other methods are used to determine the point at which freezing is complete or melting starts. Complete discussions of such methods will be found in texts on pyrometry and thermal analysis, for example: *Pyrometry,* by William P. Wood and James M. Cork, McGraw-Hill Book Co.; and *The Principles of Metallographic Laboratory Practice,* by George L. Kehl, McGraw-Hill Book Co.

against known temperatures, this makes a very good arrangement for measuring temperatures up to the decomposition temperatures of the wires—in the case of noble metals about 1500°C (2732°F). To meas-

FIGURE 3.4. Uniform cooling.

ure the temperatures of molten metals the hot junction will usually have to be protected by surrounding it with a closed end tube of fire-clay or silica.

Freezing and the Cooling Curve

For substances that do not undergo freezing or changes in specific heat, the time-temperature cooling curve will be as shown in Figure 3.4. It is roughly logarithmic. When the metal freezes, however, the freezing point will be indicated by a horizontal place in the curve if it is a pure metal, or by an abrupt change in the slope for an alloy or impure metal as shown in Figure 3.5.
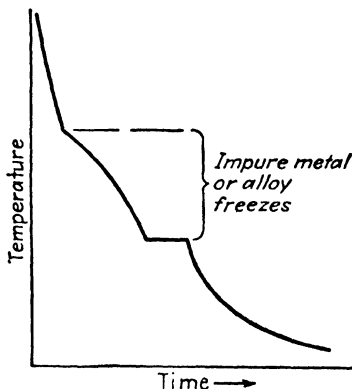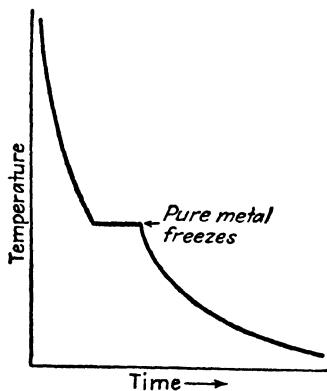
FIGURE 3.5. Cooling through a freezing temperature.

Constant Freezing Temperature

Any pure chemical element or compound is said to freeze or melt at a constant temperature. The term "constant" is used to mean, first, that during the progress of freezing no change in temperature takes place, secondly, that such a substance will always freeze at the same temperature, and thirdly, that freezing and melting take place at the same temperature.

A pure metal freezes at a constant temperature for the following reason. As the temperature is lowered to the freezing point the metal reaches a condition where it is just ready to start freezing. If, at this point, the temperature of the molten mass is uniform and the metal is pure, that is, all the same kind of substance, it would appear that every portion of the melt, however small, would be in a condition to start freezing. Any slight absorption of heat by the surroundings should cause the entire mass to become instantly solid. This it does *not* do, however, because of the abrupt energy change between the liquid and solid states of the same material. This energy change is known as *latent heat* and, in effect, means that the formation of any solid causes the unfrozen portion to be hotter so that it must be cooled some more to bring it down to the freezing point. It is evident then that freezing will start at chance locations in the molten metal and proceed only as fast as the heat produced by the freezing can be dissipated, while the temperature remains at the freezing point until the entire mass is solid.

Cooling Curves and Composition

In the case of alloys, on the other hand, another factor, composition, is involved. The composition of a pure metal cannot, of course, change during the time of freezing, but with alloys, the composition of the liquid portion can, and usually does, change as freezing progresses. It is easy to see that a change in composition *may* involve a change in initial freezing temperature since no two different pure metals freeze at the same temperature. Now if we consider a liquid mixture of the two metals, assuming such a mixture to be a solution, it might start to freeze at the freezing temperature of one of the constituent metals or at some other temperature. As a matter of simple probability it would, in general, start to freeze at a temperature different from the freezing point of either constituent metal, but its freezing temperature would be affected by the relative amounts of the two metals present and change as the proportion of the two metals changed. Hence, *if the composition of the molten portion of an alloy changes during the progress of freezing, the temperature will change also.*

Conversely: If the composition of the melt remains constant during the progress of freezing, freezing will take place at a constant temperature.

As a corollary to these propositions we may consider the relationship between the liquid and the solid portions of the freezing mass. If the composition of the liquid is changing, the composition of the solid that is forming must be different from that of the liquid. *If the*

composition of the solid is the same as that of the liquid from which it freezes, freezing will take place at a constant temperature.[4]

Alloys differ tremendously in their freezing characteristics and so, to expedite the tabulation of results and to be able to interpret them fully, we construct what is known as the composition-temperature equilibrium diagram for each pair or group of metals studied.

Let us select for study a pair of metals that have comparatively simple relationships in all their alloys. Such a pair are lead and tin,
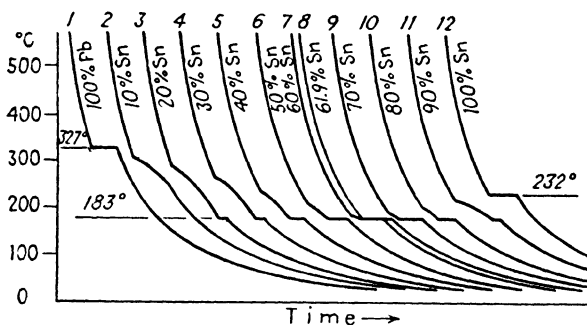
FIGURE 3.6. Cooling curves for alloys of lead and tin.

the constituents of ordinary solder. Let us take mixtures of these that vary by 10% in composition from pure lead to pure tin and make a time-temperature determination of the freezing temperature of each mixture. The series of curves will appear as shown in Figure 3.6.

The first curve shows the melting temperature of pure lead at 327°C. The next five are characterized by abrupt changes in slope at temperatures progressively lower than 327°C followed by a horizontal part at 183°C in every case (except that of 10% tin). Curve 8 has no change in slope until 183°C is reached when the curve becomes horizontal, indicating that the material freezes at a constant temperature. Further increase in the amount of tin causes the change in slope to reappear at increasing temperatures until the freezing point of tin is shown at 232°C.

Manifestly, the horizontal portion at 183°C, for all alloys containing 20% tin or more, represents the temperature at which freezing is completed and, because it is horizontal, indicates that the last portion to freeze was solidified at a constant temperature.

[4] The student should debate in his mind these propositions and others to follow, until he is fully aware of the logic underlying them. Only by so doing can he hope to comprehend metallographic ideas and learn to correlate structures and equilibrium relationships in metals.

The Binary Equilibrium Diagram

We may now omit the time dimension of our curves and plot the beginning and end of freezing on coordinate axes representing only temperature and composition (Figure 3.7). Since percentage compositions are supplementary and always add up to 100% we may consider two origins of composi-
tion, one for lead and one for tin, with 100 scale divisions between them. The temperatures at which freezing begins, as shown, by the first change in slope of the cooling curves, are plotted along the lines AB and BC, while the temperatures at which freezing is complete, as shown by the lower horizontal part of the cooling curves, are plotted on MB and BN.
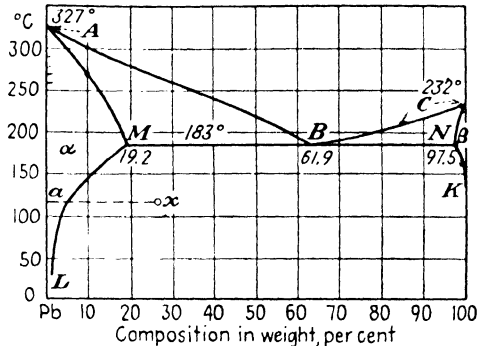
FIGURE 3.7. Lead-tin equilibrium diagram (slightly modified from the *National Metals Handbook*).

Any point on such a diagram represents a temperature and a composition of a mixture of the two substances indicated. If we choose any point for consideration, its vertical elevation above some zero level represents temperature, and its horizontal distances from the two axes represent composition. Note that for any such point there are always two horizontal distances representing composition, the sum of the two always being 100. It is also important to observe that each axis is named for the element of which it represents 100%, not for the one for which it is the origin of coordinates. Thus in the diagram shown, the axis at the left is termed the lead axis because it represents the pole for 100% lead, although it is likewise the origin for tin and percentages of tin are measured from it. When, therefore, we evaluate the percentage composition represented by a point on such a diagram, we must remember that the distance of the point from either axis represents the percentage of the element represented by the other axis. Thus, in the diagram, the distance of point x from point a on the lead axis represents the percentage of tin in the alloy.

Lines on the diagram are the loci of composition and temperature at which changes take place in the mixtures or alloys. The line ABC is called a *liquidus* because it represents the loci of compositions and temperatures of all liquid mixtures that are just beginning to freeze.

The diagram just described is known as an equilibrium diagram.[5] As used in this discussion, *equilibrium means a balance in the rates of change of materials that are reacting freely with each other.* A solid is in equilibrium with its own liquid when the rate at which the solid is melting and the rate at which the liquid is freezing are equal. This is the condition of a solid-liquid mixture at a constant temperature.

Hence, from the standpoint of equilibrium, we may consider that lines on the diagram are the loci of the compositions and temperatures of substances that are in equilibrium with other substances. The liquidus *ABC* represents the loci of compositions and temperatures of all liquid mixtures that are in equilibrium with solid mixtures.

Changes that occur in the solid, as represented by the lines *AML* and *CNK*, will be discussed in the next chapter.

QUESTIONS ON THE TEXT

1. What are slip lines?
2. What is Beilby's hypothesis of the amorphous grain boundary?
3. What is a dendrite? Describe its growth.
4. Do pure metals show dendrites in the microsection? Why?
5. What is meant by "freezing at a constant temperature"?
6. Under what conditions will a metal or alloy freeze at a constant temperature?
7. What two values are represented by a point on an equilibrium diagram?
8. What is meant by equilibrium?

SUPPLEMENTARY QUESTIONS

1. What is meant by plasticity? Is there any *nonmetallic* crystalline substance that is plastic? If so, name it.
2. Why are most solid chemical compounds brittle?
3. Describe the growth of nondendritic crystals.
4. How may crystallization take place without lowering of temperature? Consider salt crystals.
5. *Experiment:* Place a grain of granulated zinc in a drop of stannous chloride on a microscope slide and observe the reaction through a microscope. Explain what happens.
6. How does latent heat affect the freezing of (a) a pure metal; (b) an alloy?
7. Does freezing at a constant temperature necessarily indicate a pure element or a compound?

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[5] Also called a phase diagram and a constitution diagram.

The Use of the Equilibrium Diagram in the Interpretation of Microstructures

Microstructures of the Lead-Tin Alloys · The Eutectic Mixture · Solid Solutions · Cooling Curves for Solid Solutions · Solid Solubility on the Equilibrium Diagram · The Lever Relationship · Definitions

In the system of alloys discussed in Chapter III, namely lead and tin, the time-temperature cooling curves for all alloys containing 20% tin or more showed a horizontal part at 183°C. It was remarked that this indicated that the last portion of the alloy to freeze did so at a constant temperature. The reason for this is not perfectly clear from the time-temperature curve alone, nor from the equilibrium diagram, at least as far as we have considered it, and here the microscope is called upon to give a clear understanding of what happens.

Microstructures of the Lead-Tin Alloys

If we take the same series of alloys that were used for the time-temperature curves and cast them into appropriately sized specimens and prepare them for microscopic examination, we shall find an interesting series of patterns or structures. Starting with pure lead, we shall find the polygonal grain structure that is characteristic of pure metals. With certain modifications, to be discussed later, the alloy containing 10% tin will have a similar appearance and structure. When we come to the third alloy, however, the one containing 20% tin, we shall see a new type of structure. There will be dark areas and lighter areas, the dark areas having the same color as pure lead, but instead of appearing

as polygonal grains they will present a most interesting series of patterns. Some will appear as chains of rounded or elliptical areas, similar in shape, some as crosses; some resemble a string of vertebrae such as are found in the fossilized remains of prehistoric animals. These are easily explained when we remember that our microsection has cut through a system of dendritic crystallization and that instead of the dendrites growing until all available metal was used up and filling all the spaces until their boundaries looked like polygonal grains, the growth was finished before all the liquid metal was used up and another substance froze around them leaving them clearly outlined. The appearance of the figures will not be perfectly square or geometrical but will depend on the angle at which the microsection cuts through the arms and branches of the dendritic crystals.

The substance that is formed around the dendrites looks, at first glance, like pure tin, but as we examine it more carefully and with higher magnification we see that it is composed of tin with little specks of lead scattered rather uniformly through it. Now as we examine the other alloys, in order of increasing tin content, we will find that the lead dendrites become smaller, and the tin and lead mixture surrounding them increases in amount until, at 61.9% tin, the whole alloy consists of the finely divided mixture and the dendrites have disappeared altogether. As we continue with alloys of still higher tin content we get massive dendritic formations of the bright white tin that are quite similar in shape to the lead dendrites and that become larger as the tin is increased in percentage. Finally at 100% tin the surrounding mixture of tin and lead disappears and we have polygonal areas of tin.

The Eutectic Mixture

The finely divided mixture of tin and lead[1] that surrounds the dendrites, in every case, is called the *eutectic* mixture. It has a definite composition (in this case 61.9% tin and 38.1% lead). This is called the eutectic composition. It melts and freezes at a constant temperature, called the eutectic temperature, which is the lowest temperature of freezing for any mixture of these two elements.

If we refer to the equilibrium diagram of Figure 3.7, we note that the two liquidus curves slope downward from the points representing the melting temperatures of pure tin and pure lead and meet at the point representing 61.9% tin, 38.1% lead, and 183°C. This point on the diagram is known as the eutectic point.

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[1] As will be shown later, the dark material is not pure lead, neither is the white material pure tin, but to avoid confusion they can be so considered in the present discussion.

We may now consider the solidified metal. The microscope showed that the dendrites that formed from all mixtures that started to freeze at temperatures represented on line *AB* had the appearance of lead, whereas those that formed from mixtures that started to freeze at temperatures represented on line *BC* had the appearance of tin. The eutectic mixture remained as a residuum in most cases and froze last. We have, therefore, a mechanism by which to explain the behavior, on freezing, of all alloys of the series. The mechanism is as follows. Consider any molten alloy whose composition lies between 20% tin and 61.9% tin. Cool such an alloy until its temperature and composition coincide with some point on the liquidus *AB*. At this point it begins to freeze, the first product of freezing, that is, the first solid to form, being nearly pure lead. Now, manifestly, if lead is separated from a mixture of tin and lead the remaining mixture will acquire a higher percentage of tin. This will be true then of the liquid, which is the remaining mixture in this case. But according to the curve *AB* a liquid containing a higher percentage of tin than the one we started with will have a lower freezing temperature. Therefore, as freezing proceeds and lead solidifies, the liquid becoming richer and richer in tin must be cooled to a lower and lower temperature. As the temperature is thus lowered, freezing of lead continues and the percentage of tin in the liquid increases until it reaches 61.9%.

Let us leave our alloy in this condition, for the moment, and consider what would have happened had we started with a melt containing something between 61.9% and 100% tin. In such alloys the dendrites had the appearance of pure tin, indicating that pure tin was the material which was freezing first while the composition and temperature of the liquid assumed a series of values represented by points on the line *BC* (in the direction from *C* to *B*). If pure tin was freezing out, the liquid was becoming richer in lead so that eventually it must have reached the composition, 38.1% lead, 61.9% tin. But approached from the other direction, lead was freezing out of the melt that contained 61.9% tin. Therefore, from this point, further cooling causes both lead and tin to freeze simultaneously from the liquid and in the proportion of 61.9 parts of tin to 38.1 parts of lead. This is the same as the proportion of tin and lead in the liquid so that from this point on the composition of the liquid does not change and, since it is the same as that of the solid that is separating, freezing will take place at a constant temperature.

Although the solid material that is freezing at this point has the same over-all composition as the liquid, it is by no means uniform like the liquid, but in it the tin and lead are physically distinct, forming

a finely divided aggregate. This is the material that surrounds the dendrites and consists of tin with small specks of lead embedded in it. For simplicity in nomenclature we will apply the name *eutectic* to such mixtures that are composed of two or more distinct constituents and which are formed by the freezing of a liquid of eutectic composition at the eutectic temperature.

The reason why the particles of lead are embedded in the tin, and not particles of tin in the lead, in this eutectic is not simple, and no attempt will be made to explain it at this time. Eutectics fall into a variety of classes, as regards their structure, each class being characteristic of the particular alloy system in which it is found. In some eutectics the structure is that of thin plates of the two constituents packed closely together, in others of rods or elongated particles of one constituent embedded in the other. The requirement, in an alloy system, for a eutectic to occur is that the two components or elements that make up the series of alloys be mutually soluble in the liquid state in all proportions and that, in the solid state, they be insoluble or partly soluble, and, further, that small additions of either constituent to the other lower the freezing temperature of the resulting mixture.

It must be borne in mind that the dendrites that form first in an alloy whose composition is not exactly that of the eutectic always have the same composition as one of the constituents of the eutectic.

Solid Solutions

When alloys freeze, the two constituents do not always crystallize out pure. Indeed, to reconsider the lead-tin series, up to this time no explanation has been given of the observed fact that alloys with only 10% of tin did not behave like the others and showed no eutectic structure. Careful experimentation shows that solid lead may incorporate as much as 19.2% tin in a manner that parallels a liquid solution. The composition, up to this percentage, may be varied by infinitesimal amounts with no striking change in the appearance of the alloy which will, for all compositions, show the polyhedral grain structure of a pure metal. Such states of aggregation of two or more substances are quite properly termed *solid solutions*. The essential characteristics of a solid solution are:

1. It is a solid crystalline substance showing only one kind of crystal.

2. It is composed of two or more constituents distributed through each other in a manner similar to a liquid solution.

3. Its composition may be varied between limits without changing the general character of the substance.

Such a state of aggregation seems simple enough on first thought

although it will be realized that there will be far-reaching effects on the nature of the equilibrium relationships and the forms of equilibrium diagrams where liquid solutions are freezing and forming solid solutions. To understand fully these effects we must inquire a little more into the exact physical and chemical nature of the solid solution.

A striking parallel between liquid and solid solutions lies in the fact that *diffusion* of the dissolved substance may take place in the solid as well as the liquid solution. This was shown in 1896 by W. C. Roberts-Austen, a famous English metallurgist and physicist, who clamped the polished surface of a piece of lead tightly against the polished surface of a piece of alloy consisting of 5% gold, 95% lead. After a period of thirty days he took samples in the vicinity of the juncture and was able to show, by chemical analysis, that gold had diffused from the gold-bearing bar into the lead bar. Many other cases of diffusion in metal solid solutions may be observed and we do not need to resort to such tedious experiments as Sir Roberts-Austen's to see them. The equilibrium between iron and carbon, for instance, offers clear evidence of diffusion.

On the other hand, when we consider that metals are crystalline substances, and this implies that the atoms of the metal are arranged in a geometric space lattice, this solid solubility and diffusion in the solid state are not so easily understood. Without going into a complete theory we may state that there are two types of solid solutions: (1) The *substitution* type in which the atoms of the dissolved substance replace atoms of the solvent metal and in which diffusion is usually slow, even at temperatures approaching that of melting; (2) the *interstitial* type in which the atoms of the dissolved substance find their way between those of the solvent and in which diffusion is usually more rapid and the dissolved atom is generally much smaller than that of the host. As far as equilibrium is concerned it makes little difference which type we have except that in the second case the equilibrium is reached more rapidly.

Let us note that materials like glass, tar, taffy, or transparent hard candy are not solid solutions because they are not *crystalline* solids. They belong to a class of substances sometimes referred to as supercooled liquids.

When an alloy of two metals that are capable of forming a solid solution, such as lead and tin (up to 20% tin), starts to freeze, two possibilities arise. The solid solution that first forms may have the same composition as the liquid solution from which it is formed, or it may have a different composition. As a matter of simple probability it will be much more likely to have a different composition than exactly the

same composition as the liquid. In general *it will be richer in the constituent that increases* [2] *the freezing temperature of the liquid.* In the case of the lead-tin alloy, say 90% lead, 10% tin, this will be lead. We have seen that when the composition of the solid is different from that of the liquid, freezing will not take place at a constant temperature, but the temperature will change during freezing and, of course, the composition of the liquid will change during freezing. Now as a matter of experiment we find that the composition of the solid changes also, during the progress of freezing, and usually in the same general direction that the liquid changes, so that for our lead-tin alloy the tin content of both liquid and solid increases as freezing progresses. Remember, however, that the solid that started forming was richer in lead than the liquid; that is, it contained less tin than the liquid we started with.

If freezing takes place slowly so that equilibrium is constantly maintained, there will be for every liquid composition a definite solid composition. This will hold true no matter what the original composition of the liquid. Hence, on our diagram we draw a curve (AM in Figure 3.7) that represents the composition and temperature of the solid that is freezing from the liquid at all times. Such a curve is called a solidus in contradistinction to the liquidus.

Cooling Curves for Solid Solutions

Another way of locating the solidus is by the time-temperature cooling curve. This shows no flat place where the entire product of solidification is a solid solution, and all curves for the lead-tin series between 0% and 19% tin have the same general form shown in Figure 4.1. But the lower break in the curve represents the temperature at which solidification is complete. Since no lead or tin is added to, or removed from, the mixture at any time, when solidification is complete the solid will have the same composition as the original melt or liquid. But since the solid and liquid that are in equilibrium at any temperature have different compositions, the solid cannot attain this original composition until all the liquid is gone.

Solid Solubility on the Equilibrium Diagram

Having drawn the solidus and liquidus (Figure 3.7), we can now determine the composition of solid and liquid portions that will be in

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[2] Obviously, if the solid portion were richer in the constituent that decreased the freezing temperature of the liquid, that constituent being derived from the liquid would leave a liquid with a higher freezing temperature and the solid, if remelted, would have a lower freezing temperature than the liquid from which it froze. Such a condition is incompatible with our concept of equilibrium, that is, freedom of all portions of the aggregate to react with each other.

equilibrium at any temperature in the solidification range by simply drawing a horizontal line at that temperature level. Where it intersects the liquidus will show the composition of the liquid, and where it intersects the solidus will show the solid composition. At the eutectic temperature the solid solution of tin and lead is in equilibrium with a liquid composition that is, in turn, in equilibrium with nearly pure tin.[3] We may accept the obvious axiom that things in equilibrium with the same thing are in equilibrium with each other so that, at this temperature, the solid solution of tin in lead is in equilibrium with
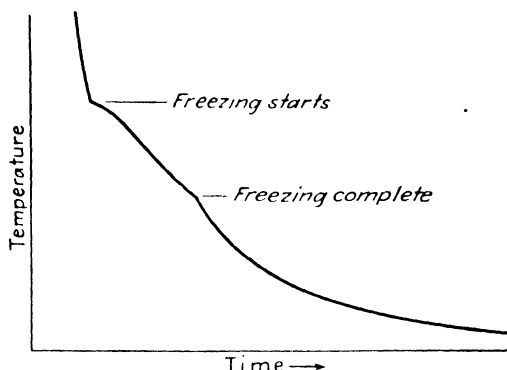
FIGURE 4.1. Freezing of solid solution.

tin. Even though the solid solution is in very intimate contact with the tin, as is also the liquid, it will not dissolve any more of it, and experiment shows 19.2% to be the limiting solid solubility of tin in lead at the eutectic temperature.

As is usual with most solutions, the solid solubility changes at lower temperatures, and careful studies of microsections of pieces cooled quickly from various temperatures enable us to plot the curve of this changing solid solubility. Such curves are *ML* and *NK* of Figure 3.7. A prominent metallurgist has recently coined the word *solvus* to apply to this type of equilibrium curve. Such curves are extremely important in the study of brasses, iron and steel, and many other alloys. They offer valuable information regarding the heat treatment characteristics of many alloys.

The Lever Relationship

Having drawn our equilibrium diagram for two metallic constituents, we discover by a simple process of reasoning that it tells us some things not suspected on first consideration. We may determine,

[3] We have used the term "tin" up to this point for simplicity. Actually the solid tin dissolves about 2.5% of lead at this temperature.

for instance, by simple measurement, the relative quantities of two phases,[4] for example, solid and liquid, that are present in a given mixture at a given temperature. Consider some temperature in the solidification range of our lead-tin system. (Figure 4.2.)
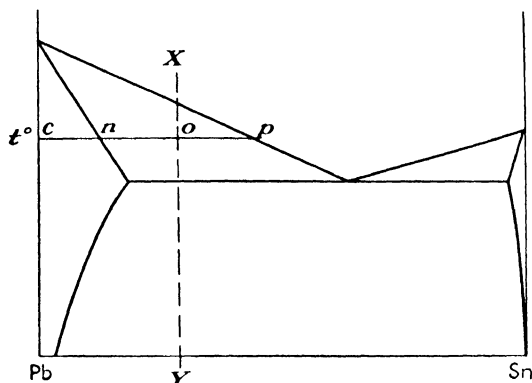
FIGURE 4.2. The lever reaction.

Assume an alloy of the composition shown by the vertical line XY. Assume that the molten alloy has cooled to temperature $t°$. Here we see that the composition of the solid phase is at n and of the liquid at p. The distance that measures the percentage of tin in the alloy is co but the per cent of tin in the liquid is cp while that in the solid is cn.

Let S = the weight of solid that has formed, the composition of which is represented by the distance cn;

L = the weight of the remaining liquid, of composition equal to cp;

$M = (S + L)$, the weight of the entire melt whose average composition is equal to co.

Then on a percentage basis,

$$(cn)S + (cp)L = (co)(S + L),$$

which simply means that the amount of tin in the solid plus the amount of tin in the liquid equals the tin in the whole mixture. Therefore,

$$(cn)S + (cp)L = (co)S + (co)L.$$

Transposing,

$$(cp)L - (co)L = (co)S - (cn)S,$$

or

$$[(cp) - (co)]L = [(co) - (cn)]S,$$

[4] See definition at the end of the chapter.

but

$$(cp) - (co) = (op),$$

and

$$(co) - (cn) = (no).$$

Therefore,

$$(op)L = (no)S,$$

or

$$\frac{L}{S} = \frac{(no)}{(op)}.$$

This is the law of the lever if we consider the line *nop* as a lever with the fulcrum at *o*. Note that it is an inverse ratio and means that the weight of the liquid is to the weight of the solid as the lever arm for the solid is to that for the liquid.

This equation gives us a simple means of calculating mixtures of all kinds. It is not confined to the liquid-solid relationships alone nor, in fact, to any particular part of the equilibrium diagram, but can be applied to any set of compositions we may select. All we need to do is to lay out a line, like the base line of the diagram, divide it into 100 divisions representing percentages, locate the compositions of two alloys on the line, and the lever law will tell us the proportions of each to use to make a mixture of any desired composition between them.

If the metallic constituents of an alloy have about the same density, the lever reaction can be used to estimate the composition from the microstructure. The best way to illustrate this is by an example. Aluminum and copper form a very complicated series of alloys, but starting with pure aluminum, we have the same kind of equilibrium diagram between aluminum and the compound $CuAl_2$ that we have for lead and tin. (Figure 4.3.)

At the eutectic temperature the solubility of copper in aluminum is 5.65%. Now if an alloy containing less copper than the eutectic mixture (33% Cu) be examined under the microscope it will show primary crystals, or dendrites, of the aluminum-rich solid solution [5] surrounded by the eutectic mixture. We may estimate the proportions of

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[5] It is true that the aluminum-rich solid solution contains less copper at room temperature than at the eutectic temperature, and of course it is examined at room temperature. However, the copper that crystallizes out of the solid solution during cooling does not, in these alloys, form an increased amount of eutectic, but rather appears as minute crystals of $CuAl_2$ scattered through the solution areas. These areas remain sharply distinguishable from the eutectic areas, and therefore the proportion of dendrites to eutectic is practically the same as it was at the eutectic temperature.

these two features. Suppose we estimate 15% of primary crystals and 85% eutectic. The distance, on the diagram, from the composition of the primary crystals to that of the eutectic is $33 - 5.65 = 27.35$. From the lever law, 15% of this distance must equal the length of the lever arm that is proportional to the amount of primary crystals. This equals
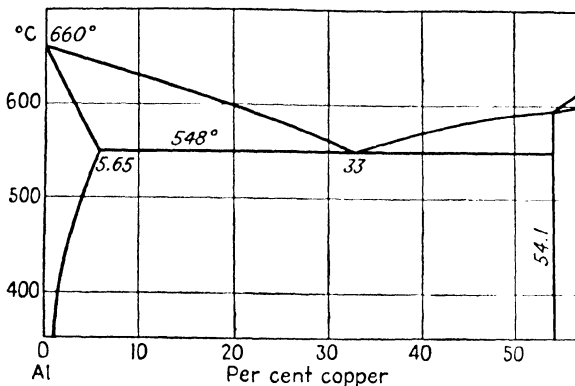
FIGURE 4.3. The aluminum end of the copper-aluminum equilibrium diagram (slightly modified from the *National Metals Handbook*).

4.10. Also, it will be remembered that this lever arm is on the opposite side of the fulcrum from the composition of the primary crystals. That is, it is adjacent to the eutectic composition (33% Cu). The composition of the alloy is at the fulcrum which is simply found by subtracting 4.10 from 33.0. Therefore the alloy contains 28.9% copper.

Definitions

Phases. The parts of an alloy that are distinguishable physically yet which in themselves contain no distinguishable parts, e.g., liquid and solid, different kinds of crystals, immiscible liquids. A more exact definition of phases will be given when the phase rule is discussed.

Primary crystals. The first crystals to form on cooling the melt. In the alloys studied so far the primary crystals are the dendrites. The eutectic mixture is made up of secondary crystals.

Aluminum-rich solution. A solid solution is said to be rich in the solvent metal. Thus in the lead-tin alloys all solid solutions of tin in lead are lead-rich solid solutions. In the aluminum alloys noted above, aluminum dissolving up to 5.65% copper forms an aluminum-rich solid solution.

QUESTIONS ON THE TEXT

1. Describe the appearance of *dendrites* in the microsection of an alloy.
2. Describe the solidification of a eutectic mixture.
3. Define a solid solution and describe two types.
4. Is glass a solid solution? Why?
5. What famous experiment demonstrated diffusion in the solid state?
6. What is a solvus curve?

PROBLEMS

Solve these problems by the lever-reaction method.

1. Derive the equation for the percentage of each constituent in terms of the lever arms and total length of the lever.

2. A lead-tin alloy contains 30% tin. It is melted and cooled until the liquid contains 40% tin and the solid contains 13% tin. What are the per cents of solid and liquid present?

3. How much copper must be mixed with 10 lb of sterling silver, containing 92% silver and 8% copper, to make a eutectic alloy containing 78% silver?

4. What per cent each of tin and lead will be required to make an alloy that shows 45% of the tin-rich solid solution and 55% of the lead-rich solid solution just below the eutectic temperature?

5. What per cent each of tin and lead will be required to make an alloy that is composed of 60% eutectic and 40% lead-rich dendrites, just below the eutectic temperature?

6. If 15 lb of eutectic solder and 10 lb of scrap tin, containing 5% lead, are melted together, what will be the composition of the resulting mixture?

7. When the alloy of Problem 6 is cooled to just below the eutectic temperature, of what will the dendrites consist and what per cent of the alloy will they occupy?

8. After slow cooling to room temperature the lead-rich solid solution contains but 1% tin and the tin-rich solid solution is practically pure tin. What per cent of each of these constituents should be present in a eutectic alloy at the eutectic temperature and at room temperature?

SUPPLEMENTARY QUESTIONS

1. How does the solidification of a eutectic mixture differ from that of a pure metal?

2. Describe the crystallization and formation of structure that should occur upon cooling lead-tin alloys of each of the following compositions as indicated by the equilibrium diagram: (a) 90% lead, 10% tin; (b) 38% lead, 62% tin; (c) 60% lead, 40% tin; (d) 25% lead, 75% tin.

3. Describe the changes that occur when the same alloys are heated to melting.

CHAPTER V

Types of Equilibrium Diagram

Conditions of Equilibrium · Diagrams Showing a Minimum Point between the Ends of the Liquidus · The Meanings of Lines and Areas on the Diagrams · Regions of Homogeneous and of Heterogeneous Equilibrium · Diagrams with a Continuously Sloping Liquidus · The Peritectic Reaction · Peritectic Microstructures · Complex Binary Diagrams

Since we have become acquainted with some of the structural devices that enter into the equilibrium relations of metals, we may now take up the various types of equilibrium diagrams that are possible. We will, for the present, deal with binary alloys, that is, alloys made up of two elementary constituents or components. Most of the information regarding alloys in general can be expressed in terms of these binary relationships, and a thorough understanding of them constitutes the most important part of metallography. The more complicated relationships, involving three or more components, find limited application among alloys, and their study, for the most part, involves only the more extended application of the ideas and principles developed in the study of the binary alloys.

Conditions of Equilibrium

If we scan the possible relationships that may exist between any two metals we find that they fall into a relatively few classifications.

1. In the molten or liquid state, the solubility may be nil, partial, or in all proportions.

2. The same may be said with regard to solubility in the solid state. Generally speaking, however, we would not expect to find much solid solubility where there was low or limited liquid solubility.

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3. The effect of each component on the freezing temperature of the other may fall into one of two classes: either may lower the freezing temperature of the other, as in our lead-tin alloys, or element *B* may lower the freezing temperature of element *A*, but *A* added to *B* raises the freezing temperature. The possible case that either might raise the freezing temperature of the other has never been found in simple, unqualified form.

For the time being let us consider only the alloys that are soluble in all proportions in the liquid state. We have then the possibilities of no solubility, partial solubility, and solubility in all proportions in the solid state, and for each of these possibilities each element may lower the freezing temperature of the other, or one may be lowered and the other raised. This makes six possible simple types of diagram.

Diagrams Showing a Minimum Point between the Ends of the Liquidus

The first three types, in which a small addition of either component lowers the freezing temperature of the other, will be modifications of the lead-tin diagram.

In Figure 5.2 we recognize the liquidus curves, the solidus curves, the eutectic point, and the solvus, or solid solubility curves. The areas denoted by the Greek letters alpha and beta (α and β) represent the ranges in composition and temperature in which the solid solutions of *B* in *A* and *A* in *B*, respectively, can exist. It is customary to use the
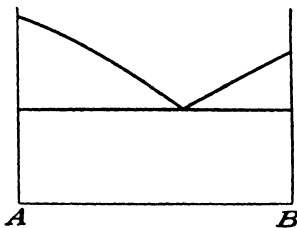
FIGURE 5.1.   No solid solubility. Type I.
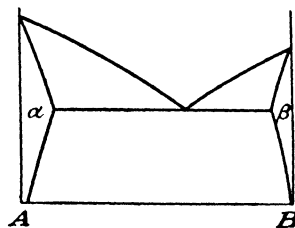
FIGURE 5.2.   Partial solid solubility. Type II.

Greek letters to denote ranges of solid solubility, the rule being that the solid solution that can exist at the highest temperature is called alpha and the solid solution ranges are called beta, gamma, delta, and so forth in order of lower maximum temperature. This rule is, however, not always followed.

In Figure 5.1 we may consider that the solidus curves coincide with the vertical boundaries of the diagram and that the alpha and beta

areas have become nil. Actually such systems probably do not exist because precise studies can usually demonstrate a slight solid solubility in such alloys.

In Figure 5.3 the alpha and beta solid solution ranges have merged.

In this case there is no real eutectic because there is only one kind of crystalline solid instead of two. The solidus and liquidus are tangent at their lowest point, and if we start with a molten alloy of exactly that composition it will freeze at a constant temperature and the microstructure will be that of a pure element, that is, polyhedral grains of one kind of crystal. This type of diagram is quite common among alloys and is characteristic of iron-nickel, iron-manganese, chromium-iron, nickel-cobalt, and many others.

FIGURE 5.3. Solid solubility in all proportions. Type III.

The Meanings of Lines and Areas on the Diagrams

So far, we have discussed the meaning of lines of the diagrams. It may be well, at this point, to consider the significance of the areas enclosed by the lines. Note that the lines represent limiting values of the compositions of certain phases in equilibrium with other phases. (See end of Chapter III.) Obviously some of the areas represent ranges of composition and temperature of certain phases; for instance, all the area above the liquidus curves represents the range of composition and temperature of liquid solutions. A point in such an area represents the composition and temperature of a liquid solution of the two elements that make up the alloy. Such a solution is in equilibrium with itself, there being no other active phase present.

Solidus lines and solvus lines enclose areas that represent ranges of solid solubility. Any isolated point in such an area represents the composition and temperature of a solid solution that is in equilibrium with itself.

Between areas representing the composition and temperature of solutions there are other areas, for instance, the space *between* a liquidus and solidus curve or the space between two solvus curves and underneath a eutectic horizontal, such as that between α and β in Figure 5.2, Type II. An alloy may have a composition and temperature represented by a point in such an area, but in this case the alloy will be composed of two phases.

The two phases represented will have compositions that depend on temperature alone. At any one temperature their compositions are fixed, and any attempt to change these compositions by additions of one or the other elementary metals will only result in changing the relative amounts of the two phases.[1]

Regions of Homogeneous and of Heterogeneous Equilibrium

Those portions of the diagram that represent the compositions and temperatures of single-phase alloys are known as regions of homogeneous equilibrium. Those portions that represent the compositions and temperatures of alloys that consist of mixtures of different phases are known as regions of heterogeneous equilibrium.

In order to acquire skill in interpreting equilibrium diagrams, it is essential to be able to distinguish, at a glance, regions of homogeneous and heterogeneous equilibrium. A few simple rules may help.

1. Areas of homogeneous equilibrium will be found above liquidus curves or below solidus curves, but a vertical line may also represent a region of homogeneous equilibrium since it represents only temperature variation in an element or compound that has no solubility for anything else in the system. Such lines are the boundary lines of the diagram shown in Figure 5.1, Type I.

2. When a region of homogeneous equilibrium has been identified, it is always separated horizontally from another region of homogeneous equilibrium by a region of heterogeneous equilibrium.

3. A horizontal line such as the horizontal connecting the compositions of the three phases represented at a eutectic temperature is,

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[1] It should be evident at this point that two phases that are in equilibrium must have compositions that lie on the boundaries of a heterogeneous field. Any deviation from this condition would be corrected by diffusion and precipitation, solution, or recrystallization. Suppose, for instance, a mixture of lead and tin powder were pressed into intimate contact and heated to, say, 180°C. Tin would straightway start dissolving in the lead until what was originally pure lead would now contain nearly 19% tin in solid solution. Meanwhile the tin grains that are left would dissolve the small amount of lead (about 2.5%) that tin can hold in solid solution. Suppose, now, we try to defeat this condition by grinding up the alloy and adding more lead powder and compressing and heating it again. The new lead grains would extract tin from the lead-rich solid solutions as well as from the remaining tin-rich grains and eventually all the lead would contain 19.2% tin in solid solution. The small amount of lead that had dissolved in the tin grains would, in proportion to the amount of tin that was removed, crystallize out carrying with it 19.2% tin. Similar reasoning can be applied to the behavior of any pair of phases in any alloy system. It should be remembered that diffusion tends to make any solution (liquid or solid) uniform in composition. If such a solution is supplied with an excess of one ingredient by the presence of another phase, its composition cannot become uniform until it is saturated with that ingredient, that is, when its composition lies on the boundary nearest that of the other phase.

of course, a region of heterogeneous equilibrium. In this case three phases are present in all alloys whose compositions lie on the line.

Diagrams with a Continuously Sloping Liquidus

The other three types of equilibrium diagram for alloys that are soluble in all proportions in the liquid state deal with those mixtures in which the component with the higher freezing temperature has its freezing temperature reduced by the addition of a small amount of the other component, and the freezing temperature of the second component is raised by a small addition of the first. In these cases the simplest diagram, Figure 5.4, is the one for solid solutions in all pro-
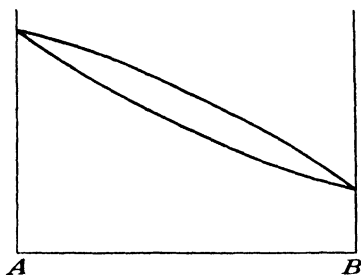
FIGURE 5.4. Solid solubility in all proportions. Type VI.
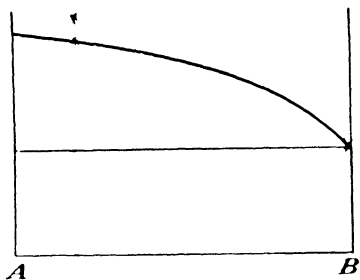
FIGURE 5.5. No solid solubility. Type IV.

portions and consists only of a solidus and a liquidus curve joined at both ends. Any alloy of this series will freeze through a range of temperatures represented by the vertical distance between the curves, and the product will be a solid solution. The noble metals and copper seem to favor this type of diagram.

Of similar simplicity is the diagram, Figure 5.5 of this series, representing no solid solubility. This consists of a liquidus that represents the composition and temperature of any liquid from which constituent *A* is freezing out pure, and a temperature horizontal that represents the freezing temperature of *B* after *A* has crystallized out completely. From any mixture we may start with in the series, constituent *A* will freeze leaving the liquid richer in *B* until it consists entirely of *B*. Then *B* will freeze as a pure element. The microstructure of such an alloy would consist of primary dendritic patterns of *A* surrounded by a matrix of *B*.

This diagram may also be considered as a limiting case of a simple eutectic diagram in which the eutectic composition is very close to the *B* axis. As a matter of fact, close study of all alloy systems that

appear to belong to this diagram indicates that they are really extreme cases of other types.

The Peritectic Reaction

The intermediate type of diagram in this series, that is, the one representing partial solid solubility of the two components, introduces
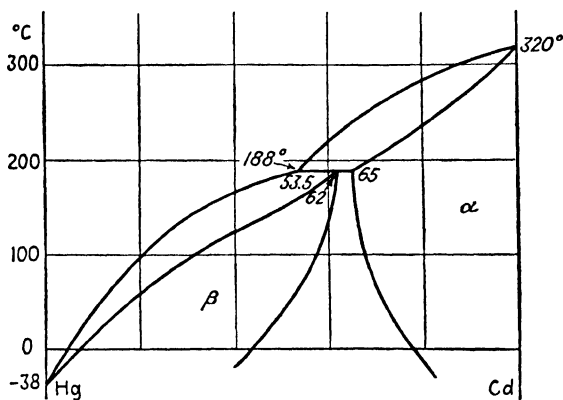
FIGURE 5.6. Mercury-cadmium equilibrium diagram (redrawn with modifications from *International Critical Tables*, McGraw-Hill, 1926). A peritectic reaction, not shown, occurs at − 34°C between mercury and beta containing 7% cadmium.

a type of relationship and equilibrium that is a little puzzling at first. To help us understand it let us choose, for discussion, a specific example in the mercury-cadmium amalgams (Figure 5.6). Let us recall the conditions described and fulfilled by this type of diagram: (1) The two components, cadmium and mercury, are soluble in all proportions in the liquid state. (2) They are partially soluble (each in the other) in the solid state. (3) Mercury, added to cadmium, lowers its freezing temperature; and cadmium, added to mercury, raises the freezing temperature of the resulting mixture.

Now that portion of the liquidus curve that represents the compositions and temperatures of cadmium alloys to which a small amount of mercury has been added is the line *ab* (Figure 5.7). From these molten alloys, solid solutions of mercury in cadmium will freeze, as
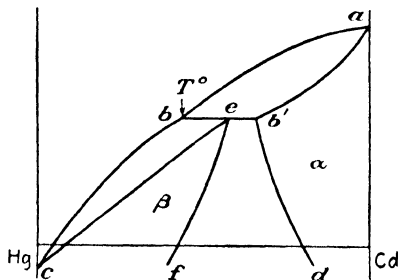
FIGURE 5.7. Partial solid solubility.

described by the solidus curve, *ab'*. These solid solutions will resemble cadmium in atomic crystal structure. On the other hand, that portion of the liquidus that represents the compositions and temperatures of mercury alloys to which cadmium has been added is the line *bc*. From these molten alloys, solid solutions of cadmium in mercury will freeze, as described by the solidus *ec,* that resemble solidified mercury in crystal structure and that are different from the mercury in cadmium solid solutions. The two solvus curves *ef* and *b'd* represent the compositions and temperatures of beta and alpha solid solutions that can exist in equilibrium with each other.

We are naturally interested in what takes place where the two branches of the liquidus curve intersect. Assuming point *b* to be the intersection, it is evident that it represents the composition and temperature of a liquid that is on the dividing line between liquids from which the alpha, cadmium-rich, solid solutions freeze, and those from which the beta, mercury-rich, solid solutions freeze. As in the case of the eutectic point, there is possible a liquid that is in equilibrium with two kinds of crystalline solid at the same time. It cannot be in equilibrium with more than two kinds of crystalline solids. The liquid, and each kind of solid will have a definite, fixed composition and, furthermore, the three kinds of phases can exist together only in the same mixture at one fixed temperature.[2] At any other temperature only two can exist together, the third having been decomposed, solidified, or melted, depending on the original composition and the temperature selected.

The situation differs from the eutectic point in that both solids contain more of the same element than the liquid. *Thus, in cooling, all the liquid cannot be used up by simultaneous precipitation of both*

[2] Logical proof of this statement may be approached from several directions but consider the following. In Chapter IV it was explained that for every liquid composition there must be a definite solid composition in the solidification range of a binary alloy. Similarly, when two solid phases are in equilibrium, each has a definite composition that changes only when the temperature changes. Now consider the liquidus curve for liquids in equilibrium with one of the solids, say the alpha solid solution, and also the liquidus curve for liquids in equilibrium with the other beta solid solution. These two liquidus curves have, in general, different slopes. Each might be extended above or below their point of intersection as the result of superheating or supercooling. The chance that, for any one of a finite number of possible alloy systems, the two curves would coincide at more than a point is infinitesimal. Hence their point of intersection represents the only temperature at which the two solid phases and the liquid can, all three, be in equilibrium.

This principle is general in all *binary* alloy systems and states that three phases can exist together in equilibrium only at a single fixed temperature. More than three solid or liquid phases are not found together in equilibrium in such systems.

solids and, of course, it could not all be used up by the precipitation of a single solid phase of different composition. Conditions for equilibrium, however, do not require that both solids precipitate simultaneously. They only require that one of the phases present be eliminated before cooling can proceed. Furthermore, the elimination of one of the phases must leave two phases whose compositions are on opposite sides of a region of heterogeneous equilibrium, which means that either liquid or alpha will be eliminated; beta will remain.

By referring to the diagrams, Figures 5.6 and 5.7, it is evident that alloys whose compositions lie between *b* and *b'* will on cooling from the melt be composed of liquid and alpha phases until temperature *T* is reached. Below temperature *T* those alloys whose compositions lie between *b* and *e* will be composed of liquid and beta phases while those whose compositions lie between *e* and *b'* will be composed of beta and alpha phases. Thus, in one case, the alpha phase has disappeared, and in the other the liquid has disappeared. In either case it is evident, considering the italicized statement in the previous paragraph, that, in some way, the liquid and alpha phases *combine* to form the new beta phase. This they do in such proportions as to produce beta phase of the composition shown at *e*. Unless the original composition of the alloy was exactly that at *e*, there will be liquid or alpha phase remaining in addition to and in equilibrium with the beta.[3] This is known as the *peritectic reaction.* It is very common in alloys, though not so well understood by many as the eutectic form of diagram. Examples of the peritectic type of diagram are found in nearly all the copper alloys, many iron alloys, and others.

Peritectic Microstructures

The peritectic reaction produces no unusual features in the microstructure, as does the formation of the eutectic. If the alpha crystals (or dendrites) are not entirely consumed, their skeleton remains will be surrounded by a matrix of the new beta material. If the original composition is such that all the alpha crystals are used up before the liquid, the final product will consist of polyhedral grains of the beta solid solution. Usually, however, equilibrium is not complete, and the alpha crystals are not all consumed even when the original composition lies to the left of point *e*, because, after being coated with a layer of the beta material, the rate of reaction between the alpha material and the liquid is greatly diminished. The beta solid solu-

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[3] This, of course, at a constant temperature. This amounts to the same as saying that a barrel filled with apples and pears cannot be emptied by removing only apples.

tion that surrounds the alpha varies in composition so that there often appears a band or rim of material surrounding the dendrites that etches and looks different from the portion of the beta material that solidified last (see Chapter VII). This is called a reaction rim.

The changes that take place upon reheating the product of the peritectic reaction (the beta solid solution) similarly tax our imagination but should be relatively obvious by this time. After the beta solution has acquired the composition at e (either by partial melting or by adjustment of its solid solubility with alpha), further heating causes it to decompose, forming a liquid and crystals of alpha. This might be likened to the charring of wood when heated, in which the wood changes to vapors of H_2O and CO_2 and charcoal.

If we apply the lever reaction to determine the relative quantities of the various materials in equilibrium before and after the peritectic reaction has occurred, we find that it confirms the interpretation we have given that part of the diagram. The problems at the end of this chapter will illustrate this.

The solutions to these problems will show that, on cooling through the peritectic temperature, the proportion of β solid solution is greater than the proportion of liquid from which it formed, so that some of the alpha solid solution was necessarily absorbed in the reaction.

Complex Binary Diagrams

The six types of diagrams just discussed comprise nearly all the kinds of relationships found in the ordinary two-component metallic alloys. However, this does not mean that every alloy system can be represented by one of these diagrams. It may require a very complex combination of several of these diagrams to represent all relationships found between some pairs of metals. A simple case is where the two metals combine in certain proportions to form compounds. There may be a simple relation between each metal and the compound. The magnesium-copper system contains two such compounds, namely, Mg_2Cu and $MgCu_2$, which involve three eutectic systems, one between Mg and Mg_2Cu, one between Mg_2Cu and $MgCu_2$, and one between $MgCu_2$ and Cu (Figure 5.8).

Again, we may have several peritectic points or peritectic points and eutectic points in the same system, for example, the zinc-aluminum diagram, Figure 5.9.[4] Here the peritectic point at 443° results in

[4] Investigators are not all in accord regarding the Zn-Al diagram, some finding no true peritectic reaction. However, the diagram shown here suits the purpose at hand and seems to fit microstructures and thermal arrests easily obtained with these alloys. For the currently accepted diagram see Figure 27.3 in Chapter XXVII on Aluminum and Aluminum Alloys.

the formation of a beta solid solution by reaction of the liquid and the gamma solid solution. Higher percentage of zinc, however, results in a eutectic between the zinc-rich alpha solid solution and the beta solid solution.
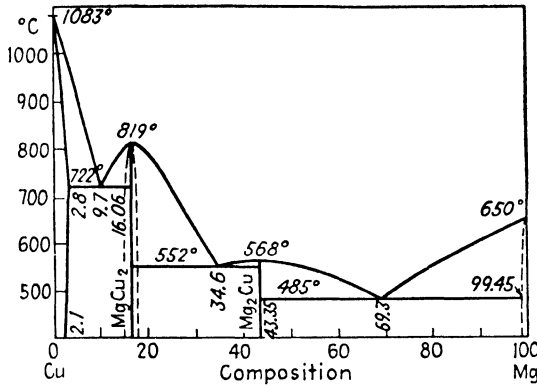
FIGURE 5.8.   Magnesium-copper (redrawn from *National Metals Handbook*).
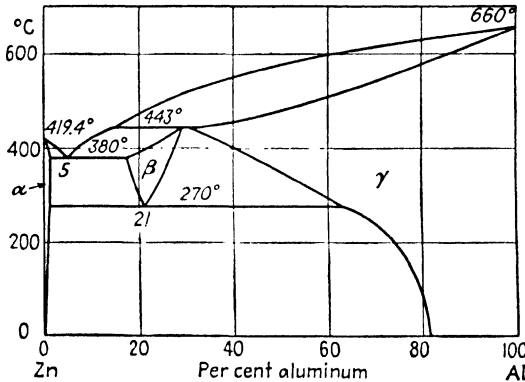
FIGURE 5.9.   Zinc-aluminum equilibrium diagram (before revision) (redrawn from *National Metals Handbook*).

The solid solubility or solvus curves add great complexity to some of these diagrams and we find relationships in the solid state even more varied than those between liquid and solid. The whole subject of heat treatment and characteristics of alloys that can be hardened by heat treatment depends on the nature of these relationships in the solid state.

QUESTIONS ON THE TEXT

1. Describe six conditions of equilibrium for metals that are mutually soluble in all proportions in the liquid state.

2. How does a minimum point differ from a eutectic point?

3. What do the oblique lines on an equilibrium diagram represent?

4. What is meant by an area of *homogeneous equilibrium?* of *heterogeneous equilibrium?*

5. Explain how to determine, from the equilibrium diagram, the compositions of two phases that are in equilibrium at any temperature.

6. Describe the progress of solidification and structural changes that take place in an alloy of Type VI (Figure 5.4). Also in an alloy of Type IV.

7. Explain, using the lever reaction, how the relative amounts of two phases vary in alloys of Type VI and Type IV during solidification.

8. Using the diagram of Figure 5.6, describe the progress of solidification of an alloy containing 55% cadmium and of an alloy containing 61.5% cadmium. Describe the structural changes that occur in each case.

9. Using the lever reaction, explain how the relative amounts of phases vary in the alloys of Question 8.

PROBLEMS

1. What is the percentage of alpha crystals and of liquid in a mercury-cadmium alloy that contains 63% cadmium, just before the reaction at 188°C has occurred on cooling?

2. What phases will be present and in what per cent in the alloy of Problem 1, just after the reaction has occurred?

3. What phases will be present in an alloy containing 58% cadmium (a) just above 188°C; (b) just below 188°C?

4. If 5 grams of mercury containing 10% cadmium is mixed with 9 grams of an amalgam containing 65% cadmium, what will be the composition of the resulting mixture?

5. How much cadmium should be added to an amalgam containing 85% mercury to bring the composition to 50% mercury if the original amalgam weighed 19 grams?

SUPPLEMENTARY QUESTIONS

1. Name two substances mutually insoluble in the liquid state.

2. Do gases ever exhibit insolubility in each other? Explain. What physical phenomenon is necessary to demonstrate insolubility?

3. Draw a hypothetical diagram for two elements, showing partial solid solubility in which the effect of either element is to raise the freezing temperature of the other.

4. Identify the regions of heterogeneous equilibrium in the magnesium-copper diagram of Figure 5.8, also in the zinc-aluminum diagram of Figure 5.9.

CHAPTER VI

The Phase Rule and Its

Application to Alloys

Methods of Approach · Statement of the Phase Rule · A System
Defined · Degrees of Freedom—F · Components—C · Phases—P ·
Use of the Phase Rule · Modification of the Phase Rule for Alloy
Systems

Methods of Approach

It has been the plan of the preceding four chapters to present the
general subject of thermochemical equilibrium as applied specifically
to metallic alloys and as limited to binary systems. The attempt has
been made to utilize the behavior of alloy systems with respect to
temperature and structural changes as a basis for developing the
mental processes involved in coordinating this behavior. Set rules
and generalities have consciously not been introduced except where
they could be demonstrated simply and logically as applying to the
subject matter at hand. A complete, albeit specific, theory based on
simple well-known physical relationships and geometrical properties
of the equilibrium diagram has been developed. The purpose of this
was to stimulate analytical thinking on the part of the student and to
avoid the pernicious habit of accepting conventional explanations
based on poorly understood and undemonstrated generalities.

This is not intended to deprecate or minimize the value of the more
general viewpoint but rather, by giving a concrete application, to
pave the way for a better understanding when the general theory is
undertaken. It is not the purpose of this book to develop a general
theory of the metallic state nor to develop any of the general physico-
chemical theory of the states of matter, either from the atomic-struc-

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ture or from the thermodynamic standpoints. However, having become acquainted with the specific relationships in metallic alloys, some of the rules and generalities laid down by physical chemistry and thermodynamics can be verified by application and, conversely, are found to be very helpful in checking the validity of specific interpretations. Such a rule is the phase rule.

Statement of the Phase Rule

The phase rule is a simple generality that is universally and precisely applicable to any physicochemical system that exists under equilibrium conditions. *It states that in any such system the number of degrees of variability equals the number of components minus the number of phases plus 2.* To understand and make use of its application, it is only necessary to comprehend fully the exact meaning of its terms. For its derivation the student is referred to the Appendix and to advanced texts in physical chemistry and treatises on thermodynamics such as Henschelwood, *Thermodynamics.*

A System Defined

It is first necessary to explain exactly what we mean by a physicochemical system. Heretofore we have referred to alloy systems in which two elementary metals were melted together in various proportions and the mixtures studied at various temperatures. More generally, we might choose any number of elementary substances as a group for study, and it would not be necessary to limit our selection to metals.

In our equilibrium diagrams we have treated the two metals as if they were the only substances in existence and their behavior was dependent on their proportions and the temperature and on no other outside influence. This we were justified in doing because, in the alloys we chose and the temperatures encountered, outside influences had very little effect. Such a group of metals is said to constitute a *system,* and the important characteristic of such a system is that all substances which go to make it up are uncontaminated and unaffected by outside influences except such as are under the control of the investigator.

In general, a system might contain gaseous elements as well as liquid and solid elements. Consequently pressure would play an important part in determining the concentrations in various domains of the system and would, therefore, have to be controlled by the investigator as well as temperature and the concentrations.

It is not necessary, in order to define a system, to consider only elementary substances. In fact, it is essential to consider in toto any compound of two or more elements if it can be shown that the com-

pound remains intact and does not decompose into other substances under any changes to which the system may be subjected.

A physicochemical system may be defined, therefore, as a *group of substances, isolated for study and free to react with one another, that may be subjected to changes in their relative amounts, temperature, and pressure at the will of the investigator.* Such a system will naturally divide itself into phases whose identity and composition will depend on the composition, temperature, and pressure of the system.

Degrees of Freedom—*F*

However, as the student will recall, there may be a certain amount of interdependence between these variables. In the case of a freezing alloy, where liquid and solid solutions are both present, the compositions of these liquid and solid solutions depend on the temperature so that if the temperature is varied these compositions will also vary in a manner described by the liquidus and solidus curves of the equilibrium diagram. Similar interdependence between temperature and composition of solid solutions has been noted. Also, we have discussed unique points such as eutectics and peritectics that can exist only at certain fixed temperatures. A similar situation exists in the constant melting or freezing temperature of a pure element or compound.

If we add pressure as another variable to the system, it is evident that a greater variety of relations between the variables will be possible.

This interdependence between the variables is subject to classification as to degree. The term *F* in the phase rule refers to this classification and means the reverse of the degree of interdependence, that is, the *degree of independence* of the variables. As usually stated, it means degree of *freedom* or of *variability*. It is always related to the number of phases present.

Specifically, one degree of freedom means that all the variables can be varied together but none of them independently without changing the number of phases. Two degrees of freedom means that the variables can be divided into two groups, one of which can be held constant while the other is varied. It makes no difference which variables are in either group. For example, consider the system water-alcohol in the presence of vapor. Assume that the mixture is in a cylinder and the vapor pressure is balanced against a piston (Figure 6.1). The variables are pressure, temperature, and composition. It is easily seen that if we hold the temperature constant, the vapor pressure will depend on the composition of the liquid so that pressure and composition must be varied as a group. Or we might hold the composition of the liquid constant by addition of alcohol as the

temperature and vapor pressure rise. In that case the pressure would depend on the temperature. Likewise, we could maintain a constant pressure if, as the temperature were lowered, the alcohol content of the liquid were raised and vice versa.

With three degrees of freedom the variables can be divided into three sets, any two of which can be varied independently while the third is held constant, or any one can be varied while the other two
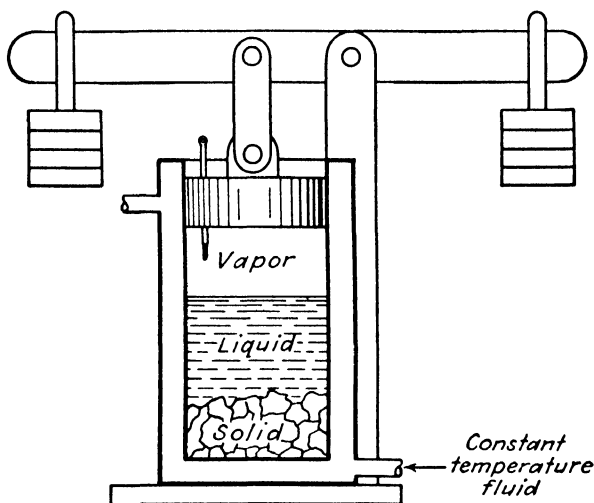
FIGURE 6.1. Schematic device for demonstrating the phase rule.

are held constant. If, in the water-alcohol system, the pressure is increased considerably, the vapor phase will disappear and the piston will rest on the surface of the liquid. Still higher pressures will have no effect on the system which now consists of only a solution of water and alcohol. Obviously, an increase in pressure, or a change in composition, or a change in temperature can be made independently of each other and need be accompanied by no other change in the system.

We cannot have more than three degrees of freedom in the water-alcohol system because we notice that as the number of phases decreases the number of degrees of freedom increases and less than one phase would mean no system.

One degree of freedom in the water-alcohol system would exist if the temperature range were such that some of the water were frozen and the piston were delicately balanced against the vapor pressure. Under such conditions all the variables could be changed simultaneously but none independently. At moderate alcohol concentrations,

say 5%, a small increase in alcohol content would lower the freezing temperature and raise the vapor pressure. If the attempt were made to keep the temperature up to where it had been, some of the ice would melt, diluting the solution to its original concentration, whereupon the vapor pressure would return to its original value.

Four and higher numbers of degrees of freedom may be found in systems containing a greater variety of substances. Obviously, since pressure and temperature must be uniform throughout the system, the variables must include independent variations in composition. If we dissolve sugar in the water-alcohol system, we can vary the sugar content independently of the water-alcohol ratio or the alcohol content independently of the water-sugar ratio.

Under certain conditions any system may have *no* degrees of freedom. Such are the freezing points of pure elements or compounds, eutectic and peritectic points, all under their own vapor pressure. Such points in cooling curves or equilibrium diagrams are known as *invariant points*.

The conventional definition for the term F in the phase rule is stated as follows:

F = the number of degrees of freedom = the number of *independent* ways in which the system can be varied without changing the number of phases.[1]

Components—C

The term C stands for components or the number of elements or compounds that go to make up the system. The conventional definition states that *the number of components is the smallest number of chemical entities*, in terms of which, without subdivision, all variations in composition of the system can be expressed. Chemical entities may be taken to mean pure elements, pure compounds, unique compositions of solutions such as the composition of a minimum point solid solution.

As stated before, we must be careful to choose the *smallest number* of chemical substances or entities in applying the phase rule. This means that such a system as Mg-Al we may consider a two-component system except at the composition of Mg_2Al where it has the properties of a one-component system.

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[1] The student must be cautioned against the naïve assumption that F means the number of things that can be varied. If a system has *any* variability, all the variables (pressure, temperature, and concentrations) can be varied. It is the number of *independent* groups into which the variables can be divided that is significant.

Phases—*P*

The term that signifies the number of phases in the system, represented by *P*, has already been partly defined (Chapter IV). The complete definition states that *the number of phases is the number of physically distinct and mechanically separable substances into which the system divides itself under the conditions imposed.* The three states of matter (gaseous, liquid, and solid) constitute separate phases but in each solid and liquid state more than one phase may exist at a time. Two or more immiscible liquids such as oil and water constitute separate phases, and each different kind of crystalline substance in a solid aggregate constitutes a separate phase.

Use of the Phase Rule

The above discussion and the illustrations presented should make it obvious that the degree of interdependence between the variable conditions of composition, temperature, and pressure under which a system may attain equilibrium will be affected by the number of components in the system and the number of phases into which it divides itself. The law connecting degree of variability (or freedom) with the number of phases and number of components is the phase rule and is stated again in symbolic form:

$$F = C - P + 2.$$

Although it is extremely simple in form and easily applied, its rigorous derivation and proof is somewhat involved and will not be undertaken here.[2] If the terms of the phase rule are evaluated in conformity with the above definitions, it will accurately fit any system in equilibrium. In some cases, confusion may arise in evaluating the terms, particularly the number of components, but if we remember to choose only those compounds or elements that undergo no decomposition within the limits of the system and yet choose the smallest number of such compounds that can be made of the elements involved and that will form a complete system under the conditions imposed, the rule will work.

Practically, the phase rule is a check on the validity of our interpretation of the effects of variations of temperature, pressure, and composition on the phase relations in a system. In applying the phase rule one should always think out the mechanism and physical results of variations imposed on the system. The procedure should be about as follows.

[2] See Appendix II.

Consider a mercury-cadmium alloy containing 63% cadmium, the temperature being 100°C. By referring to the equilibrium diagram (Figure 5.6), we see that this composition and temperature lie in the heterogeneous area between the β and α solid solution fields. If we assume that the alloy is under its own vapor pressure, there will be three phases present, and the number of components is, of. course, two. By applying the phase rule,

$$F = 2 - 3 + 2 = 1 \text{ degree of freedom.}$$

This means that only by varying all the variables simultaneously can the system be changed. From the equilibrium diagram it is evident that the compositions of the two solid phases are fixed at any given temperature. Attempts to change the compositions by addition of either component would result, when equilibrium was reestablished, only in a change in the amounts of the two phases, not their compositions. Under conditions of equilibrium, the vapor pressure is the same for both solid phases and can be changed only by changing the temperature. But obviously, if we consider the slopes of the two solvus curves, a change in temperature will also change the compositions of the solid phases. Thus the only change possible in the system is a coordinated simultaneous change in temperature, pressure, and composition.

Consider the same system at the peritectic temperature. In this case four phases are present, viz., two solids, one liquid, one vapor:

$$F = 2 - 4 + 2 = 0.$$

This indicates that the peritectic temperature is an invariant point.

Modification of the Phase Rule for Alloy Systems

Most alloy systems are held not under their own vapor pressures which are extremely low, but under atmospheric pressure. This produces the same effect as pushing the piston down to the surface of the liquid in the water-alcohol system or keeping a system consisting of solids or solids and liquids under cubic compression greater than their own vapor pressure. Elimination of the vapor phase in the first of the mercury-cadmium alloys leaves only two phases and

$$F = 2 - 2 + 2 = 2 \text{ degrees of freedom.}$$

Thus the pressure can now be set at any desired point after which the compositions of the phases will depend on temperature. Although not so obvious, if the temperature be fixed, the compositions may be changed by changing the pressure. Likewise temperature and pres-

sure may be adjusted through a range of values to maintain the same composition of the phases.

The student should apply the phase rule to systems under a variety of conditions as selected from points in equilibrium diagrams and interpret the significance of the result in each case. Problems at the end of the chapter should suggest the method of doing this.

Since, as stated above, most metal alloy systems have very low vapor pressures and are maintained under a practically constant atmospheric pressure, we will make no error if we disregard the vapor phase and pressure variable. This reduces the number of phases and consequently the number of degrees of freedom by one, so we must revise our phase rule to read

$$F = C - (P_m + 1) + 2.$$

Therefore

$$F = C - P_m + 1,$$

where P_m equals the number of solid and liquid phases.

In applying this rule to the 63% mercury-cadmium alloy we get the same results as before, because in the first case we have two solid phases, alpha and beta, so that

$$F = 2 - 2 + 1 = 1;$$

and in the second, we have two solid phases and one liquid,

$$F = 2 - 3 + 1 = 0.$$

Thus, in the first case, elimination of the vapor phase and pressure variable does not prevent us from subjecting the system to a coordinated variation in temperature and composition.

After a little practice in the application of the phase rule to specific cases we become aware of the limitations to which a system in equilibrium must be subject. We realize that in a *two-component* alloy system, not more than three phases can exist together and those only at a fixed temperature. Where two phases are present, their composition varies with the temperature if it varies at all. In the possible case of two solid phases that have no solid solubility for each other, i.e., their solvus curves are straight vertical lines, the situation is not changed. The fact that their composition cannot vary does not prevent the temperature from varying, and thus there is still one degree of freedom.

Thus, the phase rule tells us quickly and accurately what combinations of physical variables (variability), chemical variables (compo-

sition), and structural variables (phases), are possible in any system in equilibrium. It is the handmaiden, so to speak, of the equilibrium diagram and aids greatly in the interpretation of equilibrium diagrams. The equilibrium diagrams we have been studying are sometimes referred to as phase rule diagrams.

However, as noted at the beginning of this chapter we must not fail to understand clearly the actual physicochemical mechanisms by which these relationships are maintained, and we must always try to see how the actual processes of crystallization, solution, and diffusion bring a system to equilibrium.

QUESTIONS ON THE TEXT

1. What is the maximum number of phases that have been in equilibrium at one time in the alloys studied so far?

2. When a liquid solution of two components and a solid solution of the same components are in equilibrium, (a) how can the compositions of the solutions be changed? (b) what will happen to the compositions of the solutions if the temperature be changed?

3. Explain why a water-alcohol mixture in an automobile radiator will not freeze at a constant temperature.

4. What damage may occur if pure water freezes in the circulating system of an automobile?

5. Why might the damage be less with impure water or with a little alcohol even though the mixture froze?

PROBLEMS

In explaining the results of these exercises describe all possible variations that may be imposed on the system and the effects of these variations on every other variable.

Example: Apply the phase rule to a lead-tin alloy containing 35% tin at a temperature of 200°C. From the diagram (Figure 3.7), we observe that this alloy will consist of a liquid and a solid phase. The phase rule gives

$$F = C - P + 1 = 2 - 2 + 1$$
$$= 1 \text{ degree of freedom.}$$

The composition of each of the two phases is fixed by the diagram for each temperature. Consequently the temperature and composition of each phase can be varied together but not independently. Thus there is but one degree of freedom.

1. Apply the phase rule to the system H_2O when liquid and vapor are present and explain the result. Do the same for liquid, vapor, and ice.

2. Apply the phase rule (for metals) to zinc-aluminum alloys in the conditions indicated by each of the lettered points in Figure 6.2 and explain each result.
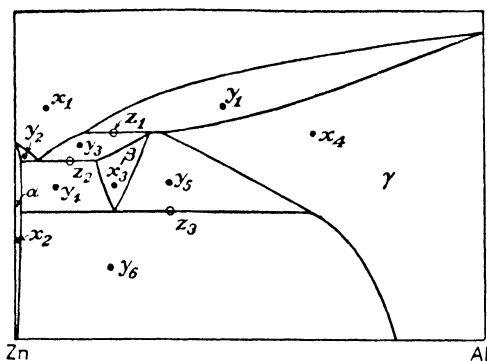
FIGURE 6.2.   The zinc-aluminum equilibrium diagram.[3]

3. Apply the phase rule (for metals) to pure zinc and pure aluminum: (a) as liquids; (b) partly solidified; (c) as solids. Explain each result.

4. Apply the phase rule (for metals) to the composition $MgCu_2$ at its melting temperature (Figure 5.8).

5. Apply the phase rule (for metals) to the minimum point (liquid and solid present) (Figure 5.3).

[3] See footnote 4, Chapter V, p. 48.

CHAPTER VII

Deviations from Equilibrium; Metastable Equilibrium

Time, a Factor in Equilibrium · Diffusion and the Composition Gradient · The Freezing of a Solid Solution · The β Curve · Dendritic Segregation · The Case for Slow Diffusion · The Cure for Segregation · Metastable Structures–Eutectic · Uncompleted Peritectic Reactions · Multiple-Phase Structures · Metastability · Supercooling or Undercooling

Time, a Factor in Equilibrium

The significance of the last statement in the preceding chapter becomes apparent when we realize that true equilibrium is almost never attained in solid metallic alloys. Just as a cooling body approaches the temperature of its surroundings as a limit, but theoretically never actually reaches that temperature, so changes in alloys that require diffusion in the solid state would theoretically take infinite time for completion. In the case of the cooling body the approach to room temperature is rapid if the temperature difference between that of the body and the surroundings is great, but as this difference diminishes the rate of cooling also diminishes. Only because the temperature of the surroundings does not remain absolutely constant and slight variations finally mask or obscure a small difference in temperature between the cooling body and the surroundings, does the body *appear* to have cooled off completely.

Diffusion and the Composition Gradient

Diffusion in the solid state is usually slow, even between high concentration differences. Its rate depends on the composition difference and the nature of the materials involved. The composition difference

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and distance through which it is realized can be summed up in the term *composition gradient* which is defined as change in composition per unit distance.

In Chapter IV, it was pointed out that diffusion is usually more rapid in interstitial type solid solutions than in the substitution type. Carbon, for instance, forms an interstitial solid solution in hot steel and diffuses much more rapidly than does nickel through the same kind of metal. Even so, in a piece of pure iron placed in contact with powdered charcoal the carbon content will show an increase to a depth of but ⅛ inch in about eight hours if the temperature is held at 1700°F. In the substitution type solid solutions diffusions may be so slow as to require days, weeks, or even years at elevated temperature to show microscopic evidence of change. .

Diffusion in liquid or gaseous states of matter is aided by convection currents. Added to this is the fact that molten metals are usually at a higher temperature than in the solid state, so equalization of composition goes on with much greater rapidity. In fact, for ordinary cooling rates we can usually *assume* that equalization is instantaneous and the entire liquid phase is in equilibrium with the surface of the solid with which it is in contact.

The Freezing of a Solid Solution

In our analysis and study of equilibrium diagrams, we have assumed that where two phases were in equilibrium, they maintained equilibrium by changes in compositions when the temperature changed. Of course, this required diffusion and, as we have just explained, diffusion may be very slow where solid phases are concerned. However, we were justified in our original viewpoint because it showed us the direction in which these changes took place. Actually, the over-all composition of a solid solution that is forming as the result of cooling a liquid solution is quite different from the equilibrium composition shown by the solidus curve.

This can be nicely demonstrated on a theoretical basis by considering the progress of cooling of a solid solution through its solidification range of temperature.[1] As a concrete example, let us consider a solid solution of nickel and copper, these being soluble in all proportions in the solid state. The equilibrium diagram is that shown in Figure 5.4 and listed as Type VI. It is reproduced here as Figure 7.1.

Let us choose an alloy containing, say 40% copper (60% nickel),

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[1] This demonstration is worked out, as applied to iron-carbon alloys, by Frederico Giolitti, in *Heat Treatment of Soft and Medium Steels*, translation by E. E. Thum and D. G. Vernaci, first edition, McGraw-Hill Book Co.

indicated by the vertical dotted line x_1x_2. Heretofore, we have reasoned that, equilibrium being maintained at all times, solidification took place upon cooling from temperature t_1 to temperature t_2. During this change in temperature, the point representing the composition and temperature of the liquid phase moved along the liquidus curve from L_1 to L, and the point representing the composition and tempera-
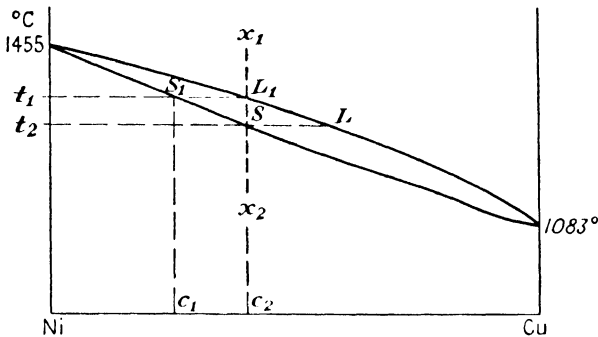
FIGURE 7.1. The nickel-copper equilibrium diagram (redrawn from *National Metals Handbook*).

ture of the solid phase followed the solidus curve from S_1 to S. This is based on the assumption that each phase was of uniform composition throughout.

However, it is easy to see that the first crystals of metal to form at t_1 had the composition shown by the point at S_1, which we may call c_1 as measured on the base line. Since the final composition of the alloys when the solidification is complete is c_2, and since the solid phase is of uniform composition, these first crystals must have become richer in copper as cooling proceeded. This must have been accomplished by diffusion of copper from a source richer in copper than these first crystals. This source may have been either layers of metal deposited on and enveloping the first crystals or the liquid itself, which in some cases may have remained in contact with parts of the first crystals.

Now we must consider the more practical situation where diffusion is slow and the composition of the solid phase is not uniform. Under these conditions the second increment of solid to form will be less pure (contain more copper) than the first, the third less pure than the second, and so on. It will simplify our reasoning if we assume, for the time being, that *no* diffusion takes place in the solid phase and that each increment remains as formed and has a composition that was in equilibrium with the liquid at its temperature of formation.

If we refer to the diagram (Figure 7.2), we see that the first increment to solidify has the composition c_1, the second c_2, the third c_3, etc. If no diffusion takes place, each increment of solid cools to room tem-
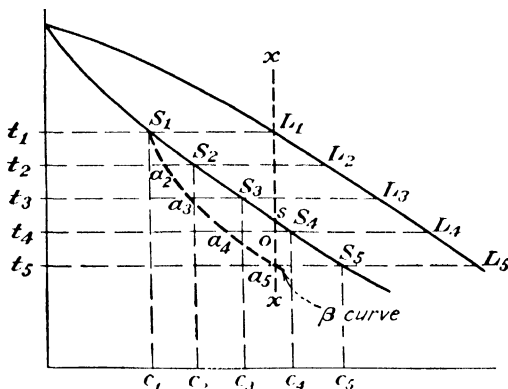
FIGURE 7.2.   Solidification without diffusion.

perature without change in composition, and we finally have a heterogeneous solid composed of layers, or domains, of continually varying composition.

The β Curve

At any temperature such as t_3, the solid that forms (S_3) will be in equilibrium with the liquid (L_3). But the average composition of the entire solid phase will be less in copper than the composition shown by the solidus for that temperature. Actually, this average composition will be somewhere between that of the first crystals to form, represented by the vertical S_1c_1, and the point on the solidus curve at that temperature. Thus for each temperature we can assume [2] an average composition that will move to the right as the temperature drops, though not so rapidly as the solidus. Connecting the points representing these average compositions we get the line $S_1a_2a_3a_4a_5$. This curve represents the average composition and temperature of the solid phase as solidification proceeds. For convenience and in conformity with Giolitti's development we may call it the β curve.

We may still apply the lever law to determine the amount of liquid and solid present at each temperature but must remember to use the point on the β curve, i.e., the average composition of the solid phase,

[2] If we knew the mathematical equation for the solidus curve, we might calculate where this average point should lie. However, for the present purpose this is entirely unnecessary as long as we know that such an average exists between c_1 and the solidus.

as a basis for our calculation rather than a point on the solidus. At temperature t_4, for instance, the proportion of liquid to solid is

$$\frac{L}{S} = \frac{a_4 o}{o L_4}.$$

It should be perfectly obvious that *solidification is not complete until the β curve intersects the vertical representing the original composition (line $x_1 x_2$)*. The point s, where the original composition vertical intersects the solidus, has *no special significance* under these conditions. The last solid to form (S_5) has the composition c_5 and the last remaining liquid was represented at L_5. When solidification is complete the solid phase is composed of material ranging in composition from c_1 to c_5.

Dendritic Segregation

This range in composition in an alloy is known as segregation. It will, in general, follow dendritic patterns since it is the result of solidification, and solidification proceeds by the development of dendrites. It is the reason that solid solutions usually show dendritic patterns in their microstructures although they are single phase alloys. This type of segregation is often re-ferred to as dendritic seg-regation. Figure 3.3 shows this dendritic segregation clearly.

The Case for Slow Diffusion

Since the progress of cooling has been estab-lished under conditions where diffusion maintains the solid phase uniform in composition at all times and also under conditions where no diffusion takes place, the intermediate

FIGURE 7.3. Solidification with some diffu-sion. Homogenization by reheating.

case, where diffusion is slow but not lacking, is easily understood. The diagram in this case is as shown in Figure 7.3.

The lines $S_1 c_1$, $S_2 c_2$, etc., representing the composition and tempera-ture of successive increments of solidified metal, slope to the right as solidification proceeds. This indicates that each increment becomes

enriched in copper by diffusion from without. Under these circumstances the β curve, representing average composition of the solid phase, slopes more to the right and comes closer to coincidence with the solidus than in the case of no diffusion. The more rapid or complete the diffusion or the slower the cooling the more nearly will the β curve coincide with the solidus.

After the alloy has all solidified, i.e., below t_5, all increments will change in composition so as to approach as a limit that of the original alloy (x_1x_2). The lines become more nearly vertical as the temperature becomes lower, indicating that diffusion is slower at lower temperatures.

The Cure for Segregation

At the temperature represented by the base line of the diagram, the composition of the alloy varies from c_1 to c_5. A long sojourn at this temperature would reduce this difference in composition, but it can be reduced more rapidly if we reheat the alloy somewhat. As pointed out by Dr. Giolitti, no part of the alloy is now as rich in copper as the last solid to form, which is S_5, so we may now heat the alloy above t_5, its final solidification temperature, without causing it to melt. Diffusion is more rapid at higher temperatures, and this is one way of overcoming dendritic segregation.

Alloys that are cast into ingot form and subsequently rolled into bars or shapes are more easily "cured" of dendritic segregation than are castings. This is true because regions or domains of different composition are stretched out into long thin fibers in the rolled alloy. These fibers, packed closely together, present sharper composition gradients over shorter distances than before, making diffusion more rapid and effective in reducing such gradients. This is one reason why rolled alloys are, in general, sounder and more reliable than cast alloys of the same general composition.

Metastable Structures—Eutectic

The effects of dendritic segregation are far reaching in the behavior of all alloys where solid solutions are involved. Let us reconsider the lead-tin diagram, Figure 7.4. If an alloy containing less than 19% tin (such as x_1x_2, Figure 7.4) be cooled quite rapidly, it is evident that the β curve may be directed as if to cross the original composition vertical below the eutectic temperature. Therefore, when the eutectic temperature t_2 is reached, some liquid will be left. Assuming, as always, that diffusion is complete in the liquid phase, the liquid will be of eutectic composition and will freeze as a eutectic at temperature t_2.

A long sojourn just below the eutectic temperature will, of course, allow diffusion to proceed in the solid phases, eventually removing the evidence of a two-phase eutectic. However, in many similar alloys, this effect causes eutectic structures to appear where they should not, and makes the accurate determination of maximum solid solubility at the eutectic temperature somewhat difficult.

FIGURE 7.4. Eutectic structure produced by dendritic segregation.

Uncompleted Peritectic Reactions

In the case of a peritectic point the effect becomes still more pronounced. The product of the peritectic reaction, that is, the beta phase, nearly always coats or surrounds the first-formed dendrites, thus separating them from the liquid. Under these conditions, the reaction must take place entirely within the beta phase and can proceed only by virtue of diffusion. This greatly slows up the reaction and reduces the chance of its being completed in any limited time. This was pointed out in Chapter V.

The effect of an uncompleted peritectic reaction is to divide the alloy into two separate systems. One system is the residual alpha crystals in equilibrium with the inside surface of the beta envelopes; the other is the liquid in equilibrium with the outside of the beta envelopes. Further cooling causes continued precipitation of beta from the liquid as in a simple system of the type shown in Figure 7.3.

Multiple-Phase Structures

The antimony-tin equilibrium diagram of Figure 7.5 may be used to show some of the possibilities that result from these retarded transformations. The alloy x_1x_2 (25% tin) starts to freeze at t_1. At 425°C, if equilibrium has been maintained, it consists of 14 parts liquid and 25 parts alpha crystals. If the reaction were completed at this temperature the final product would consist of 10 parts alpha crystals and 14 parts beta crystals. The structure should be skeleton (partly dissolved) dendrites of alpha surrounded by a matrix of beta.

However, under ordinary conditions of cooling, the alpha crystals would average less than 11% tin at 425°C so there would be more

than 14 parts of liquid left. This liquid has the composition shown at y. It should, theoretically, freeze entirely to solid beta by the time 325°C is reached, but again, cooling rapidly will prevent the composition and temperature of the solid from keeping up to the solidus curve so that there may still be a small amount of liquid left when 325°C is reached. The formation of the beta-prime phase would probably use up all the remaining liquid, but it is within the realm of possibility that it would not and that a trace of liquid would survive until 246° was reached to form some gamma phase.

FIGURE 7.5. Antimony-tin equilibrium diagram (redrawn with modifications from *National Metals Handbook*).

Thus we might have alpha, beta, beta-prime, and gamma phases present (and some liquid momentarily) in a two-component system. Such a situation is impossible under equilibrium conditions according to the phase rule:

$$F = 2 - 5 + 1 = -2.$$

The explanation is, of course, that these are not equilibrium conditions.

Metastability

Materials that are in a condition of suspended change are said to be metastable. The alloy just discussed, if cooled rapidly to room temperature, would probably undergo no further change in months or years, yet we feel confident that there is a latent tendency to change. As a matter of fact, long anneal at sufficient temperature to promote slight diffusion will cause solution and reprecipitation to proceed until only the alpha and beta phases remain.

Metastability has many forms, many of them so firmly established that very unusual conditions are necessary to bring about a change to true stability. Many organic compounds, particularly living organisms of all kinds, are metastable, especially if we include the oxygen of the air in the system. To break down these systems to their stable forms it may be necessary to heat them to their ignition temperature, whereupon they are converted to the stable compounds, viz., CO_2, H_2O, N_2, etc.

Supercooling or Undercooling

The undercooling of a liquid below its *initial* freezing temperature is a case of metastability. Most liquids can be held but a fraction of degree below their freezing temperatures, and then but momentarily, when they quickly and spontaneously revert to their stable form, that is, start to freeze. There are a few cases, however, such as sodium thiosulphate (hypo) where the liquid form can be held many degrees below its freezing temperature for long periods of time. Solidification (crystallization) can be started by adding some of the crystalline material to the undercooled liquid. As soon as the stable form starts to develop in an undercooled substance, it starts to get warmer, indicating that heat is evolved.

Long sojourns at temperatures below 0°C will cause pure tin to revert to a powdery form that is stable at low temperatures. This is known as tin disease and takes place very slowly. Ordinary tin at low temperatures is metastable.

The iron-carbon alloys that form steel contain a compound whose formula is Fe_3C. This compound has been shown to be metastable, and it breaks down with the evolution of heat into graphite and iron.

Undercooling to a slight degree may be assumed in all cases of solidification and, in fact, in all cases of phase change. We may reason thus in the case of freezing. For example, imagine a liquid that has been cooled just to its freezing temperature but that has not started to freeze. Because of the latent heat of freezing, heat must be subtracted from the liquid to promote actual freezing. But subtracting heat from the liquid involves lowering the temperature. The formation of solid will raise the temperature again as explained in Chapter III, but it is apparent that the solid will not form until the liquid has been slightly undercooled.

If, in analyzing the changes that take place in alloys when they are heated and cooled, we can keep before our minds the equilibrium relationships, the retardations that depend on diffusion and the principles of metastability and undercooling, it will help us to visualize the actual mechanisms by which these changes occur.

QUESTIONS ON THE TEXT

1. What is meant by a composition gradient?
2. Do composition gradients persist in liquids? Why?
3. What is meant by the beta curve?
4. At what temperature will a solid-solution alloy actually complete its freezing?

5. What is dendritic segregation? How may it be reduced?

6. Explain why a peritectic reaction is often incomplete and describe a *reaction rim.*

7. Define metastability.

SUPPLEMENTARY QUESTIONS

1. Using the lead-tin diagram (Figure 3.7) show that an alloy containing 10% tin might cool in such a way as to show dendrites of solid solution surrounded by the eutectic structure.

2. Can a eutectic structure be segregated? Explain.

3. Must a peritectic reaction always take place at the peritectic temperature?

4. A solid-solution alloy is melted and then cooled until its temperature and composition lie on the solidus curve. It is held at this temperature. Describe its process of solidification, at this temperature, by diffusion.

5. Show that the solidification of a solid solution might be considered a series of peritectic reactions differing by infinitesimal steps in temperature and composition of the phases involved.

CHAPTER VIII

The Iron-Carbon Alloys

Importance of Iron-Carbon Alloys · Names of Iron-Carbon Alloys · Composition Limits · Methods of Production · The Terms Acid and Basic

Importance of Iron-Carbon Alloys

From the standpoint of mankind, the most important alloys, the extended use of which is the distinguishing feature of our present civilization, are the iron alloys. And we may well emphasize the word *alloys* in this case because the element iron, alone and in pure form, has played a minor role. True, modern developments have found important use for the very pure forms of iron such as ingot iron; and wrought iron,[1] another pure form, has been used very generally and was a forerunner of steel. But the truly great advances upon which modern transportation and commerce depend are the advances in the arts and sciences involved in the manufacture and use of alloys of iron and carbon. We are justified in calling alloys, mixtures of the metal iron with the non-metal carbon that have been melted together and cast, since, in accordance with the definition given in the first chapter, they have metallic characteristics and serve useful purposes.

To account for the great utility of the iron-carbon alloys we may list a few important factors.

1. We find in these alloys the widest variation in physical properties of any of the common alloys. These variations can be effected by small but easily controlled variations in composition and simple variations in heat treatment.

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[1] Actually, wrought iron is not as free from all impurities as some steels, but the impurities that it contains are controlled only to the extent that they are reduced to as low a value as possible and their effect on the strength of the metal is small.

2. The cost of iron-carbon alloys is low and the materials required in their production are very plentiful.

3. Certain unique characteristics distinguish iron alloys from all other metals, notably their magnetism and their ability to change their crystal structure when heated or cooled past a certain temperature range (700° to 900°C) which is known as the transformation temperature range.

Names of Iron-Carbon Alloys

Before proceeding with the structure and equilibrium of the iron-carbon alloys, it will be well to acquaint ourselves with the names given the various kinds and some of their commonly observed characteristics. Everyone is familiar with the terms iron, steel, cast iron, wrought iron, ingot iron, and some others without, perhaps, knowing much about their distinctive features. Although such groups as the American Society for Testing Materials and the American Iron and Steel Institute have given these terms more or less rigorous definitions that would have to stand in a legal dispute, such definitions are somewhat cumbersome and not very enlightening to the student. A brief discussion of the materials to which these terms apply will give a better understanding of their meaning.

From the standpoint of the chemist or scientist, the element iron means but one thing, that is, the element whose atomic weight is 55.84, symbol Fe. Hence, very pure commercial forms of the metal are also called iron with certain modifying adjectives to indicate the method of manufacture such as wrought iron and ingot iron.

On the other hand, it is only natural that the product of the primary reduction of iron ore should be termed iron, regardless of how impure it may be, even after it is remelted without essential changes in composition. So we have pig iron and cast iron.

When, however, the material undergoes a special process by which it is partly purified and the composition is accurately controlled to produce properties that are different from those of the pure iron and of the cast or pig iron, it is given the name steel.

Composition Limits

A difficulty arises when we attempt to set composition limits for these materials. This is not due to any inherent uncertainty regarding the proper place for such limits in pure iron-carbon alloys but rather to the fact that commercial steels are not pure iron-carbon alloys but contain appreciable amounts of other elements in varying proportions. The maximum amount of carbon permissible in the steel classification will depend on the amount of these other elements.

The element that has the most influence on the properties of iron is carbon, so that it is the one whose limits should be set for the various classifications. The maximum amount of carbon that will be found in any iron-carbon alloy is less than 7%. Most pig irons, however, contain less than 4% carbon. One of the essential characteristics of steel is its ability to harden on quenching in water from a high temperature. This effect is maximum at about 0.80% carbon but is made use of in alloys that contain as much as 1.60% or 1.70% carbon. However, any alloy containing less than 2.20% carbon may be called steel according to standard definition.

Methods of Production

Many iron-carbon alloys are classified according to the process by which they are produced. The blast furnace is the apparatus in which iron ore is initially reduced, or smelted. The product of the blast furnace is called pig iron, regardless of whether it is actually cast into the small horizontal bars called pigs, or cast into some useful form, or not cast at all, but kept molten in a large container until it can be charged into an open-hearth furnace or bessemer converter, to be made into steel. If it is allowed to solidify as pigs, however, and then charged into a foundry furnace, such as a cupola or air furnace, remelted without purification, and cast into its final form as a useful article, it is called cast iron.

Another distinction based on method of production is the distinction between wrought iron and ingot iron. *Wrought iron* is produced by the puddling process in which it is finished in a plastic, semi-molten state, the impurities, in non-metallic form, being mixed in with the iron as a melted slag. The mass of iron plus slag is then squeezed between rolls so that much of the slag is eliminated, leaving the iron in quite pure form with residual streaks of slag scattered through it. *Ingot iron,* on the other hand, is produced in the open-hearth furnace and finished molten, in which state it is cast into ingots which are rolled out into bars, sheets, and other forms. It is one of the purest commercial forms of iron and analyzes at least 99.9% Fe.

Steels may be classified according to either composition or method of manufacture. We have, on the one hand,

Low-carbon or soft steels	0.07 to 0.30% carbon
Medium-carbon steels	0.30 to 0.60% carbon
High-carbon or hard steels	0.60 to 1.40% carbon

Alloy steels are those containing alloying elements other than carbon in amounts sufficient to produce marked changes in the properties of the metal.

On the other hand, we may speak of acid open-hearth steels, basic open-hearth steels, electric steels, crucible steels, bessemer steels.

The Terms Acid and Basic

The distinction between basic and acid steelmaking processes is based on the kind of slag that is formed with the oxidized impurities from the metal. Briefly, it is necessary to add such materials in a steelmaking process as will form a fusible mass with the oxides that form when the impurities in the iron are burned out. This is primarily to make it easy to get rid of these impurities and to make a liquid, glassy cover to prevent excessive oxidation of the metal after the desired amount of purification has been accomplished. The chemical nature of the slag, however, has much to do with the purification of the metal. Particularly, most of the phosphorus and, to a lesser extent, the sulphur, often present in pig iron, are removed if the slag is rich in lime, that is, *basic;* but these are not removed if the slag is rich in silica. Silica, chemically, is the anhydride of silicic acid, so slags rich in silica are called *acid* slags.[2]

Often the terms acid and basic are applied to the furnaces themselves. Here we must consider the effect of the slag on the walls and bottom of the furnace. Acid materials attack basic materials and form fusible slags with them, so it would not do to make an acid slag in a furnace lined with basic refractories such as dolomite and magnesia. Likewise, we could not retain a slag high in lime in a furnace lined with silica sand and brick.

Since basic slags cause phosphorus and sulphur to be lowered in the metal, it would seem that the basic processes were to be desired instead of the acid processes, and it is true that they are essential where the ores and pig irons contain appreciable quantities of these impuri-

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[2] The following table may help to recall some simple chemical reactions in the non-metallic materials encountered in steelmaking:

Acid or Base	Molecular Formula	Anhydride	Molecular Formula of Anhydride
Silicic acid	H_2SiO_3	Silica	SiO_2
Calcium hydroxide	$Ca(OH)_2$	Lime	CaO
Magnesium hydroxide	$Mg(OH)_2$	Magnesia	MgO

Alumina, Al_2O_3, may be considered as the anhydride of either aluminum hydroxide, $Al(OH)_3$,

$$2Al(OH)_3 = Al_2O_3 + 3H_2O,$$

or of aluminic acid, H_3AlO_3, by a similar reaction. Alumina behaves as a base in the presence of strongly acid materials and as an acid in the presence of strongly basic materials.

ties, but where very high-grade ingredients are available, such as Swedish charcoal pig iron and high-grade ores, the acid open-hearth is capable of producing a slightly higher grade of steel than the basic process. This may be due to the physical character of the slag, which is more glassy in the acid process than in the basic, resulting in less entrapped material in the metal.

To summarize, we may list the iron-carbon alloys in order of purity as follows:

1. Pure elementary iron (purest)
2. Vacuum distilled electrolytic iron
3. Ingot iron
4. Wrought iron
5. Low-carbon or mild steel
6. Medium-carbon steel
7. High-carbon steel or tool steel
8. Semisteel
9. Cast iron
10. Pig iron (least pure)

QUESTIONS ON THE TEXT

1. Describe two characteristics of iron alloys that are lacking, or almost so, in other metals.
2. Name four commercial materials to which the name iron is applied.
3. What is steel?
4. How much carbon may steel contain?
5. What is meant by an acid slag? by a basic slag?
6. What is meant by acid pig iron? basic pig iron? acid steel? basic steel?

SUPPLEMENTARY QUESTIONS

1. List five articles that are made of soft and malleable steel.
2. List five articles that are made of tough steel of high strength.
3. List five articles that are made of very hard steel.
4. List five articles made of cast iron.
5. Why do blacksmiths prefer wrought iron for hammer welding?
6. List five characteristics of the pure element iron.

The Equilibrium Relations of Iron and Carbon

The Iron-Carbon Equilibrium Diagram · The Carbide of Iron, Cementite · Interpretation of the Diagram · The Allotropy of Iron · The Eutectoid Point · The Eutectoid Structure; Pearlite · Phases and Structures

The Iron-Carbon Equilibrium Diagram

After a rather hasty introduction to the different kinds of iron-carbon alloys, our interest will naturally be directed toward the methods of manufacture of these materials and to a study of their properties. First, however, let us keep alive the ideas that were developed in the earlier chapters by taking a glance at the iron-carbon equilibrium diagram.

The diagram, Figure 9.1,[1] is complex. Although it is based on a 100% relationship between iron and carbon, we note that there are no alloys containing more than 6.67% carbon represented. As a matter of fact there is nothing definitely known about alloys higher than this in carbon because, if they can exist, they form at too high a temperature to be studied. However, we recognize a eutectic point of 4.3% carbon and 1130°C. Also, at 0.50% carbon and 1492°C we note a peritectic point. This latter was discovered in recent years and has little bearing on the behavior of carbon steels. It is helpful in studying the behavior of the stainless steels which contain large amounts of chromium.

There is a solidus curve, whose position shows us that at the eutectic temperature (1130°C) the iron dissolves carbon up to 2.0%. Below this temperature, the solid solubility (solvus) curve, falling off to the

[1] As was noted in Chapter VII, this diagram is based on the existence and assumed permanence of the metastable compound Fe_3C.
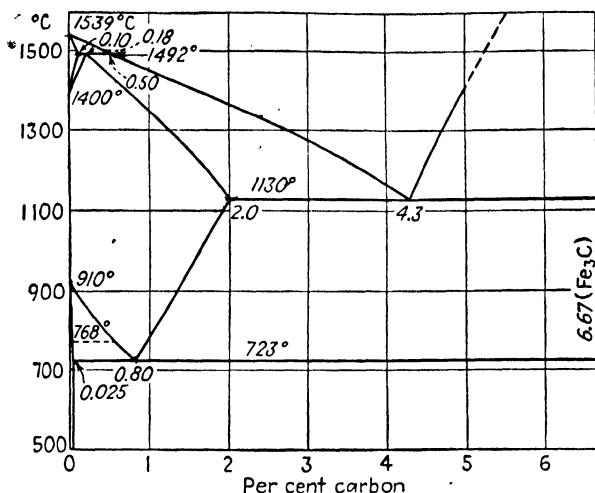
FIGURE 9.1. Iron-carbon diagram (metastable) (redrawn with modifications from *Metal Progress Data Sheets*, Am. Soc. Metals).

left, indicates that the carbon is less soluble in the iron as the temperature becomes lower.

The Carbide of Iron, Cementite

On the other side, i.e., to the right of the eutectic point, we find a vertical at the composition 6.67% carbon. This composition fits the compound Fe_3C, which we may calculate[2] from the molecular and atomic weights:

Atomic weight of Fe......................... 56
Multiply by................................. 3
                                            ———
                                            168

Atomic weight of C 12
Molecular weight of Fe_3C 180

$$\% \text{ carbon in } Fe_3C = \frac{12}{180} \times 100 = 6.66 \cdots$$

In all steels the carbon that is not present in solid solution is held as part of this compound. This compound can be distinguished under the microscope as a hard white material that does not etch as rapidly as the rest of the metal and so stands in slight relief on the section.

[2] The student may calculate this value to a higher degree of accuracy using the atomic weight of iron as 55.84.

The compound Fe_3C, iron carbide, is given the name *cementite*. It has a fixed composition and dissolves neither iron nor carbon in solid solution.

It is important to understand the relation between iron at the eutectic temperature (1130°C) and this compound, cementite. Iron dissolves carbon at that temperature, forming a solid solution. It can dissolve as much as 2.0% carbon under these conditions. The iron may derive the carbon for this solid solution from cementite, if it is in contact with it. The cementite, when deprived of part of its carbon, is decomposed and changed to the same solid solution, containing not more than 2.0% carbon. In alloys containing more than 2.0% carbon, there will always be cementite present below the eutectic temperature. The solid solution has the same space lattice as iron, which is face-centered cubic at the eutectic temperature.

If we start with a solid solution of carbon in iron containing 2.0% carbon at 1130°C and cool it, the carbon content of the solid solution will be lessened. The carbon does not, however, separate out as such but takes some iron with it to form the compound Fe_3C (cementite). Hence, the equilibrium, in pure iron-carbon alloys up to 6.67% carbon, is not between carbon and iron but rather between cementite and iron.

Interpretation of the Diagram

Superimposed on the iron-cementite relationships are some changes in the element iron itself. Pure iron can exist in two different kinds of space lattice, and the kind that it assumes depends upon the temperature. Furthermore, one of these kinds dissolves carbon, or cementite, while the other does not. This is further complicated by the fact that the temperature at which the alloy changes from one space lattice to another depends on the amount of carbon present.

We can understand it readily, however, if we follow the diagram of Figure 9.1. Iron at its melting temperature (1539°C) has a body-centered cubic space lattice. This has a maximum solubility for carbon of only 0.10% at 1492°C. If we cool pure iron to 1400°C, it changes spontaneously to the face-centered cubic lattice and assumes a much higher solubility for carbon. At 910°C, however, the space lattice changes back again to the body-centered cubic form and the carbon solubility drops to 0.025%.

Using the same diagram, but with the values omitted and letters to indicate positions, Figure 9.2, we find the vertical line *aehi* represents pure iron at temperatures below its freezing point. From *a* to *e* it is body-centered cubic; from *e* to *h* it is face-centered cubic; and below *h* it is again body-centered cubic.

Starting with pure iron at its freezing temperature, the first portion of the liquidus curve, *ad*, represents the compositions and temperatures from which solid solutions of carbon in body-centered iron are freezing as described by the solidus *ab*. The next section of the liquidus, *dg*, represents those liquids from which solid solutions of carbon in face-centered iron whose compositions and temperatures are de-
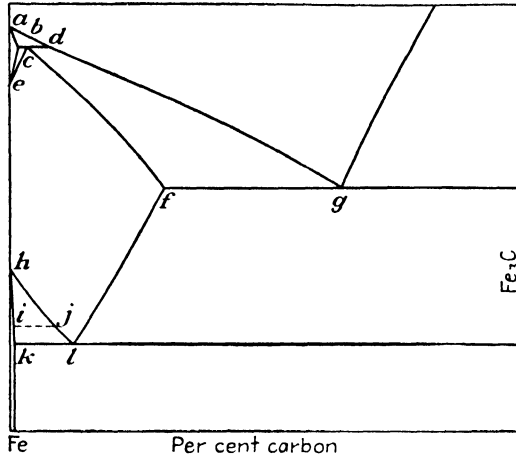
FIGURE 9.2. Iron-carbon alloys.

scribed by the solidus *cf* are freezing. The section of liquidus to the right of the eutectic point represents compositions and temperatures of liquids from which cementite separates on cooling.

The curve *fl* is the solvus that represents the compositions and temperatures of *solid solutions of carbon in face-centered iron* that are in equilibrium with the compound Fe_3C (cementite) below the eutectic temperature.

The area *abe* represents all possible compositions of carbon in body-centered iron between the temperature at *a* and that at *e*, and area *ecfljh* gives all possible compositions of carbon in face-centered iron between the temperatures of *c* and of *l*.

The Allotropy of Iron

The ability of a metal to exist in several different forms at different temperatures and to change these forms abruptly at certain critical temperatures is termed allotropy. The different forms are termed allotropic forms and differ from each other in physical and chemical properties. Heat effects, such as latent heat, and density changes are

noted on heating or cooling through the critical temperatures where these allotropic forms change.

A few other metals besides iron exhibit such changes. They are not especially common, however. Tin is a notable example. This changes its form at 18°C and again, to a third form, at 161°C. The change at 18°C on cooling is accompanied by so much expansion that it causes the ordinarily bright, soft metal to break up into a fine gray powder.

The allotropy of iron has been recognized for centuries. Needless to say, it was not first discovered by x-ray observations, nor was it associated with any knowledge of microstructures. Yet any blacksmith that ever hardened a cold chisel is, and has been since the time of Tubal Cain, acquainted with the fact that iron has vastly different properties at temperatures above a red heat from those below. A certain temperature was found at which there was a peculiar heat effect known as recalescence whereby heated pieces of steel, on cooling, reached a dull red heat and then suddenly brightened up and spontaneously became hotter. From above the temperature at which this happened, steel could be hardened by quenching in water, but no hardening was effected when the steel was quenched from just below this temperature, and a previously hardened piece of steel would be completely softened by quenching just below this temperature.

The first scientific studies of the allotropy of iron were made by means of our old friend, the time-temperature cooling curve. Latent heat is always developed upon cooling through an allotropic change, so such changes are indicated by changes in the slope of the curve. The cooling curve for pure iron, from its freezing temperature down to room temperature, is as shown in Figure 9.3.

FIGURE 9.3.   The allotropy of iron.

The rather slight effect at 768°C has never been thoroughly understood. It represents the temperature at which iron loses its magnetism on heating and regains it on cooling. There is no known structural change, however, that can be associated with the heat effect.

The effect at 910°C is the important one from the standpoint of the heat treatment of steel. This effect is due to the fact that the material changes, on cooling, from the face-centered to the body-centered space

lattice. This change is accompanied by a 1.2% increase in volume. If we remember that the face-centered iron that can exist above this temperature dissolves carbon, up to about 2.0%, whereas the body-centered iron into which it changes upon cooling below 910°C can dissolve but 0.025% carbon, we can see that profound changes in the character and properties of the metal must take place as the result of heating or cooling through this temperature.

The different allotropic forms of iron are designated by Greek letters. These should be thoroughly understood and memorized as they are always referred to in discussions of metallography and heat treatment.

Alpha iron is the low-temperature form that exists below 768°C. It has the body-centered cubic space lattice and is magnetic. Its solubility for carbon is less than 0.025%.

Beta iron exists between 768°C and 910°C and is non-magnetic body-centered cubic iron. Its solubility for carbon is similar to that of alpha iron.

Gamma iron exists between 910°C and 1400°C. It is face-centered cubic, non-magnetic, and dissolves carbon up to 2.0% at 1130°C.

Delta iron is in all respects similar to beta iron except that it exists from 1400°C to the melting temperature.

Any piece of iron undergoes these changes of form on heating or cooling, and as often as the heating or cooling is applied.

The temperatures at which these changes occur are fixed for pure iron but, as might be suspected, as soon as some carbon is dissolved in the gamma iron, the temperatures of transformation are changed. Specifically, the effect of a small amount of carbon is to *lower* the temperature of the *gamma-beta* change and to *raise* that of the *gamma-delta* change. The extent to which the carbon affects the temperature of the change depends upon how much carbon is present, so that we can plot a curve on the equilibrium diagram that represents the compositions and temperatures at which these changes occur. Such a curve will be a solvus curve because it will represent the compositions and temperatures of solid solutions of carbon in gamma iron that are in equilibrium with alpha, beta, or delta iron, as the case may be.

In the equilibrium diagram of Figure 9.2, the curve *hj* represents the compositions and temperatures of solid solutions of carbon in gamma iron that are in equilibrium with beta iron. That is, when we cool any solid solution represented by a point on the line *hj*, beta iron will actually form as little crystals embedded in the gamma iron solid solution.

Since the magnetic change occurs entirely in the body-centered iron

which does not dissolve carbon,[3] its position will not be affected by the carbon content of the steel but will always occur at the same temperature as long as beta or alpha iron are present. This fact will be represented by the horizontal line *ij*.

The line *jl* represents the compositions and temperatures at which gamma iron is in equilibrium with alpha iron. A similar line of reasoning may be applied to the changes involving gamma iron and delta iron.

The Eutectoid Point

We see that the line *hjl* represents the compositions and temperatures of solid solutions from which beta or alpha (both body-centered) irons would form on cooling. We remarked in a previous section that the curve *fl* represented the compositions and temperatures of solid solutions that were in equilibrium with cementite, or Fe_3C. The point *l* in Figure 9.2 is, therefore, similar to a eutectic point where a solution is in equilibrium with two new crystal forms or phases. The difference is that in this case the original solution is a crystalline solid solution whereas the eutectic was formed from a liquid solution. Because of the similarity, yet acknowledging the difference in the two cases, this kind of point is termed a eutectoid point.

The Eutectoid Structure; Pearlite

Eutectoid points are common in alloy systems, and the structures of the resulting alloys, which we will refer to as eutectoid structures, or simply eutectoids, are as varied as those of eutectics. In the case of the iron-iron carbide eutectoid the structure is beautifully laminated, being composed of packs of thin plates of Fe_3C and alpha iron. The microsection shows this as groups of fine, parallel, but wavy lines, somewhat resembling fingerprints, or sand ripples on a beach.

These parallel lines, quite evenly spaced, often produce light interference effects similar to those described in the first chapter in the derivation of Bragg's law for x rays. These effects give an iridescent appearance to the section, after polishing and etching, much like the appearance of shells or mother-of-pearl, whose appearance is also due to fine striations or laminations. For this reason metallurgists refer to this laminated structure as pearlite.

[3] In this statement we are neglecting the small amount of carbon necessary to saturate the beta phase (less than 0.025%). Careful measurements show a difference in the temperature of the beta-alpha transformation for irons containing between 0% and 0.025% carbon.

Phases and Structures

The iron-carbon alloys, on account of their commercial importance, were among the first substances studied from the equilibrium diagram standpoint. The different allotropic forms and solid solutions have been given names which are in general use. Where the pure allotropic form is referred to, the Greek letter is used, as described above, but for the solid solutions and less pure commercial alloys other names are applied.

Ferrite. Alpha or beta iron containing customary impurities such as manganese (up to 1%), nickel, copper, phosphorus, and sulphur, in solid solution.

Austenite. The solid solution of carbon in gamma iron, also with other dissolved impurities.

Cementite. This may also be considered as an impure form of Fe_3C or iron carbide with manganese, chromium, or other carbides, crystallized together.

Ledeburite. The eutectic (formed at 1130°C, 4.3% carbon) between austenite and cementite.

Pearlite. This name is applied to the eutectoid, whether pure or not, and regardless of whether or not any iridescence is seen in the microsection. Indeed, under certain circumstances it can be obtained, not laminated, but as grains of cementite embedded in a matrix of ferrite, in which case it is called spheroidite (formerly granular pearlite).

Before studying the microstructures of the various forms and compositions of steel we will inquire into the physical properties of these ingredients from which we may be able to understand some of the reasons for the properties of the steels themselves.

Ferrite is quite soft and ductile. It has a tensile strength of about 40,000 psi and can be drawn into wire. It hardens considerably in the drawing process, however, and must be annealed every four or five passes through the dies or it will break. Commercial irons that are nearly pure ferrite are rivets, sheets, soft wire such as baling wire, nails, pipe, and a variety of other articles of common or domestic use. Ferrite is not amenable to heat treating and will not harden materially on quenching.

Austenite is a form of iron-carbon alloy that is not obtainable pure at ordinary temperatures. In the temperature range in which it is stable, 723° to 1492°C, it is extremely soft and malleable and can be worked indefinitely without rupture. This working does not harden it,

in which respect it behaves like a wax. Forging and rolling operations are performed in this range of temperature.

Cementite is not obtainable in massive pieces in pure form but, judging by irons that are composed largely of cementite, it is practically non-metallic in its hardness and brittleness, and would be comparable to porcelain and rock-forming materials. It is not possible to determine its tensile strength because of this brittleness. It is the chief constituent of white cast iron, an infrequently used material. Its presence in steel serves, as we shall see later, to reinforce the soft ferrite so as to give any desired combination of toughness and hardness.

Pearlite is a good example of this reinforcing effect. It is composed entirely of ferrite and cementite, and the cementite actually constitutes one eighth of the total mass, the other seven eighths being the soft ferrite. Yet, whereas ferrite may have a tensile strength of but 40,000 psi, the pearlite will test about 120,000 psi or three times as much. Steel rails are composed almost entirely of pearlitic steel.

QUESTIONS ON THE TEXT

1. Sketch from memory the iron-carbon equilibrium diagram with correct values of composition and temperature at all intersections. (*Note:* Ordinarily it is not recommended that equilibrium diagrams be memorized. However, the importance of the iron-carbon alloys makes imperative a ready knowledge of their equilibrium relationships.)

2. Label each area of homogeneous equilibrium in the iron-carbon diagram with the name of the phase indicated.

3. Label each area of heterogeneous equilibrium with the names of the phases that are indicated.

4. Define cementite; ferrite; pearlite.

5. What is meant by allotropy? Describe the allotropic changes that occur in iron.

SUPPLEMENTARY QUESTIONS

1. Redraw the iron-carbon equilibrium diagram to the Fahrenheit temperature scale.

2. Redraw the iron-carbon diagram on the basis of per cent Fe_3C instead of per cent carbon, calculating the new values.

3. Describe the phase changes that should take place in the following iron-carbon alloys when they are cooled from the liquid state to room temperature: (a) 0.20% C; (b) 0.80% C; (c) 1.40% C; (d) 2.50% C.

4. How many closest neighbors does an iron atom in the gamma form have? in the alpha form?

CHAPTER X

Structures of Slowly Cooled Iron-Carbon Alloys

The Structure of Cast Iron versus Steel · The Importance of the Behavior of Austenite on Cooling · Microstructures Resulting from the Slow Cooling of Austenite · The Effect of Carbon on Microstructure · Estimation of Mechanical Properties from Microstructure · Iron-Carbon Eutectic Alloys; White Cast Iron · Gray Cast Iron · The Cause of Graphitization · Malleabilization of White Cast Iron · The Widmanstätten Structure

The Structure of Cast Iron versus Steel

It is easily seen from what has been described so far that alloys containing less than 2.0% carbon will have been entirely in the form of austenite at some stage in their history. Alloys containing more than 2.0% carbon will always contain some eutectic (ledeburite) made up of austenite and undissolved cementite (Fe_3C). This cementite surrounds, as a matrix, the particles of austenite in the eutectic mixture, and the eutectic mixture in turn envelopes the dendrites of austenite, Figure 10.2. Thus cementite is continuous in the structures resulting from all alloys containing more than 2.0% carbon. In such structures the properties, as regard hardness and brittleness, will be largely those of the continuous material, namely, the cementite. It would seem, therefore, that a good dividing line between cast iron and steel would be 2.0% carbon because above this percentage the metal is brittle at all temperatures below its melting point, and below this percentage there is always a temperature, or temperature range, in which the metal assumes the soft, malleable, austenitic form.

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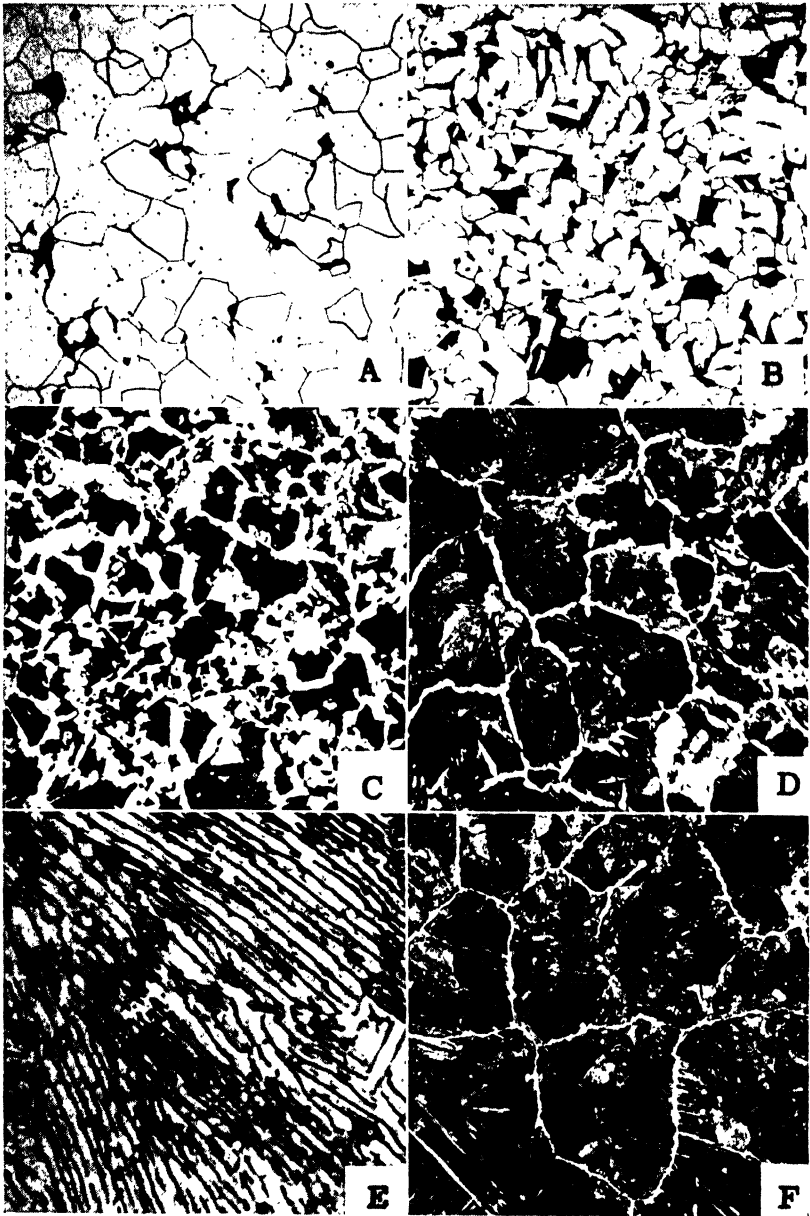
FIGURE 10.1. The effect of carbon content on the structure of slowly cooled steels. (A) 0.10% carbon, 100×; (B) 0.20% carbon, 100×; (C) 0.50% carbon, 100×; (D) 0.70% carbon, 100×; (E) 0.80% carbon (eutectoid), 2000×; (F) 1.40% carbon, 100×.
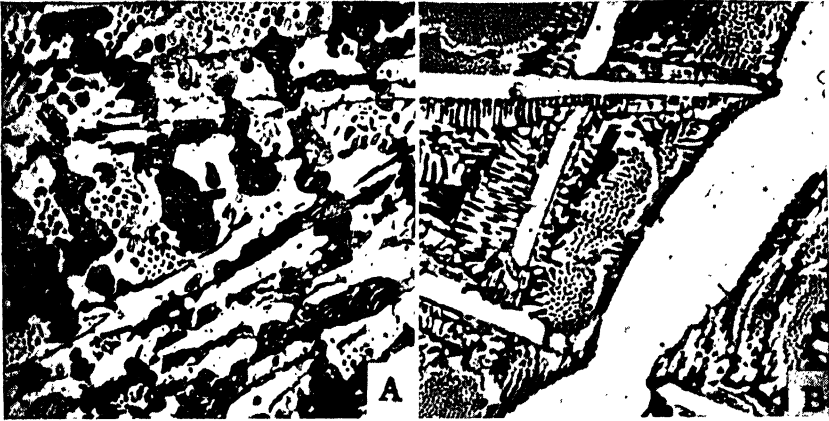
FIGURE 10.2. Cast irons showing eutectic structure, 100×. (A) Hypoeutectic iron, 2.5% carbon; (B) hypereutectic iron, 5.00% carbon.

The Importance of the Behavior of Austenite on Cooling

In the behavior of austenite on cooling, on the other hand, we find the reasons for all the variability in the properties of steel. Austenite, as we have seen, undergoes decomposition on cooling below 723°C, the decomposition products always being ferrite and cementite. The proportion and physical arrangements of these products depend upon the composition of the alloy.

Since austenite is a solid solution of carbon in γ (face-centered) iron, we can assume its structure to be the same as that of a pure metal, namely, polyhedral grains joined at grain boundaries. Reference to the equilibrium diagram reminds us that austenite containing just 0.80% carbon decomposes entirely upon cooling to form pearlite, the finely laminated mixture of ferrite and cementite. From austenite containing *less* than 0.80% carbon, *ferrite* precipitates upon cooling between 900° and 723°C until the residual austenite contains 0.80% carbon. From austenite containing *more* than 0.80% carbon and up to 2.0% carbon, *cementite* precipitates on cooling between 1130° and 723°C leaving a residual austenite of 0.80% carbon. The residual austenite, in all cases, changes to pearlite.

The material that precipitates above 723°C, either ferrite or cementite, has a tendency to crystallize at the grain boundaries of the parent austenite. This is quite different from the formation of dendrites from a liquid solution. In this case, the newly formed material envelopes the grains of residual austenite, separating them from each other. The microsection shows this as a white network of either ferrite or cement-

ite surrounding the grains of pearlite into which the residual austenite has transformed, Figure 10.1.

Microstructures Resulting from the Slow Cooling of Austenite

Substituting the network for the dendrites, we have then, in steels containing less than 2.0% carbon, a series of structures similar to those of the lead-tin series of alloys. Very low carbon gives a structure consisting of polyhedral grains of ferrite. At isolated spots in the midst of these we find small patches of pearlite. As we examine steels of increasing carbon content, the pearlite patches become larger and the ferrite appears to form the network around them. With still higher carbon contents the ferrite network becomes finer until, at 0.80% carbon, it disappears altogether. Above 0.80% carbon we find the network again, but now composed of cementite. This can be distinguished from the ferrite by its hard appearance and its bright whiteness. In doubtful cases it may be definitely distinguished by etching the specimen in boiling sodium picrate.[1] In this solution the cementite turns brown whereas ferrite will remain colorless.

The Effect of Carbon on Microstructure

Having become acquainted with the equilibrium relations in iron-carbon alloys and some of the microstructures, let us inquire briefly into the relationships between the composition and microstructure of slowly cooled steels. This is the first step in understanding the reasons for the variety of physical properties of steel.

Pearlite, the eutectoid composed of ferrite and cementite, and formed by the decomposition, on cooling, of austenite, contains about 0.80% carbon. At magnifications not exceeding 100 diameters it does not usually show separate laminations of ferrite and cementite but, owing to fineness of subdivision, has a dark uneven structure resembling a pile of leaves (Figure 10.3). Occasionally, the dark areas have iridescence or color. When the composition of the steel is such that there is extra ferrite or cementite present, the dark pearlite areas stand in sharp distinction to the bright metal or compound. By estimating the relative areas of the pearlite and of the ferrite, or cementite, and using the lever reaction, it is quite a simple matter to calculate the per cent carbon in the steel.

As an example, let us calculate the per cent carbon in a steel that appears to be about 45% pearlite and 55% ferrite. The ferrite, at the eutectoid temperature, contains about 0.025% carbon. Although, as a

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[1] Etch for 10 minutes in a boiling solution composed of 2 grams of picric acid, 25 grams NaOH, and 100 milliliters of water.

result of cooling from 723°C to room temperature, part of this may have precipitated as Fe_3C, it will, due to slowness of diffusion, not have migrated to the pearlite areas but will still be associated with the ferrite. The total distance on the composition scale from this point to the composition of pearlite is 0.80 − 0.025, or 0.775. Forty-five per cent
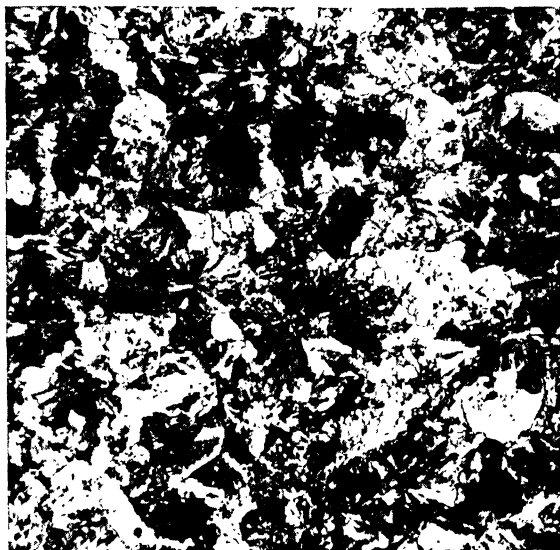
FIGURE 10.3. The leaf-pile structure of pearlite at low magnification, 100×.

of this distance equals 0.349, which is the length of the lever arm that represents pearlite. Adding the 0.025, we get 0.374% carbon, which is the amount present in the steel.

Steels containing less carbon than 0.80% will have structures consisting of a network of ferrite surrounding islands of pearlite. Such steels are called *hypoeutectoid* steels. Steels that contain more than 0.80% C are called *hypereutectoid* steels and their structures are characterized by a network of cementite surrounding islands of pearlite. In estimating the compositions of hypereutectoid steels from their microstructures, we must take into account the composition of cementite, viz., 6.67% carbon.

Suppose we have a steel that shows 90% pearlite and 10% Fe_3C. The total length of the lever is 6.67 − 0.80. This equals 5.87; 90% of this equals 5.28. Since this is the arm that represents the proportion of pearlite, it starts at the composition of cementite and extends to the left. So, to get the position of the fulcrum we must subtract 5.28 from 6.67, leaving 1.39. This is the per cent carbon in the steel.

Let us remember that these results are for slowly cooled steels. There is no such easy way to estimate the structures and compositions of heat-treated steels. These will be studied in later chapters.

Estimation of Mechanical Properties from Microstructure

Early writers in metallography attempted to draw conclusions regarding the physical and mechanical properties of slowly cooled steels from the appearance of the microstructures. They reasoned that each structural feature should contribute its own properties in such a way that the value, in the aggregate, for any specific characteristic such as tensile strength should be the summation of the values for that characteristic in each structural feature, multiplied by the percentage of that feature.

Thus, assuming the tensile strength of ferrite to be 40,000 psi and that of annealed pearlite to be 105,000 psi, the equation

$$\text{tensile strength} = 40,000\,\frac{F}{100} + 105,000\,\frac{P}{100}$$

should give the correct value for any hypoeutectoid steel. F and P represent the percentages of ferrite and pearlite, respectively.

If we carry the results farther, since ferrite and pearlite comprise all of a hypoeutectoid steel,

$$F = 100 - P.$$

Therefore,

$$\text{tensile strength} = 40,000 + 650P.$$

From the lever reaction we may calculate,

$$P = 130.7C - 4.575,$$

where C is per cent carbon. Substituting this value for P, we get

$$\text{tensile strength} = 37,026 + 84,955C,$$

by which the tensile strength may be estimated from the carbon content.

However, such calculations are only of speculative interest. Values can be found for the tensile strength of annealed pearlite that range from 76,000 to over 110,000 psi, and for annealed ferrite, between 35,000 and 48,000 psi. Later studies have shown great variations in strength due to grain size, spacing of the pearlite lamellae, and traces of impurities such as oxygen, hydrogen, and nitrogen, that are not usually determined in routine analysis.

A rather elaborate system of estimating the effects of heat treatment

on alloy steels from their chemical composition and grain size has been worked out by M. A. Grossmann.[2] The values are of an empirical nature based on many hundreds of tests and require a complete chemical analysis and grain-size measurement for their application.

Iron-Carbon Eutectic Alloys; White Cast Iron

As was stated in the beginning of the chapter, when the carbon exceeds 2.0% there will be no temperature at which the alloy will be composed entirely of austenite, but some cementite will persist up to the melting temperature. If the alloy contains more than 4.3% carbon there will, of course, be present some primary crystals of cementite. These usually occur as long white platelike areas in the microsection, although they may occasionally appear as hexagonal or rhombic areas. They indicate prismatic crystals.

The presence of the undissolved eutectic cementite inhibits any malleability in such alloys, and for this reason, alloys containing more than 2.0% carbon are considered to be in the cast iron classification. Only occasional alloys with this much carbon and with other alloying elements are classified as steels. Cast irons in which the carbon is present as cementite and as described by the metastable equilibrium diagram (Figure 9.1) are known as white cast irons.

In parallel with the steel nomenclature, the white cast irons may be classified as hypoeutectic, eutectic, or hypereutectic. The significance of such terms should be obvious from the diagram. Hypoeutectic and hypereutectic cast irons are shown in Figure 10.2.

The microstructures of these white cast irons are somewhat complex. In Figure 10.2A the dendritic material formed above 1130°C is austenite containing 2.0% carbon. This is surrounded by the eutectic mixture consisting of small spheroids or rods of similar austenite embedded in the cementite matrix. This eutectic mixture is called ledeburite. However, at lower temperatures, all the austenite loses carbon which forms additional cementite. At 723°C the austenite should contain 0.80% carbon. This forms pearlite upon slow cooling. Hence the final structure of such alloys will consist of either dendrites or cementite crystals surrounded by a eutectic pattern. Both the dendrites and the discontinuous phase in the eutectic will have changed to pearlite, and since pearlite is an aggregate of ferrite and cementite, it is evident that ultimately any carbon steel or white cast iron must consist of these two phases.[3]

[2] "Hardenability Calculated from Chemical Composition," by M. A. Grossmann, *Trans. Am. Inst. Mining Met. Engrs.*, **150**, 127 (1942).
[3] The student should now be able to analyze and describe all the structures and structure changes that occur in the slow cooling of any iron-carbon alloy from the liquid state to room temperature.

White cast iron has little practical use by itself. It is too hard for ordinary machining and too brittle for structural purposes. It is interesting from a purely theoretical standpoint because it completes the iron-carbon equilibrium diagram. It forms the chilled portion of chilled castings, producing a hard surface where wearing properties are demanded.

Gray Cast Iron

A more useful form of cast iron is gray cast iron. In this material, all or part of the cementite or pearlite has decomposed, leaving the carbon as crystalline masses of graphite. This graphite is usually present as thin warped sheets or flakes which appear to break up the continuity of the metal (Figure 10.4). When gray iron is fractured, the fracture has a dark gray to black appearance which is due to the

FIGURE 10.4.   Gray cast iron, 100×.

fact that the path of the fracture is mostly through the graphite flakes.

When cast iron is entirely gray, that is, completely graphitized, the metallic matrix is ferrite. This results in an aggregate that exhibits some toughness, although, because of the broken up character of the ferrite, it will not show any appreciable ductility. Such material has a low coefficient of friction and makes a fair bearing material. One of its

important uses is in engine cylinders. It has ideal machining characteristics.

When not all the carbon is in the form of graphite, but some remains as pearlite, the fracture may show silvery areas interspersed with the dark gray areas. This is called *mottled cast iron* and is somewhat harder than the gray cast iron. Several grades of cast iron are used in which the classification depends upon the degree of graphitization of the carbon.

The Cause of Graphitization

It has been definitely established that graphite is the stable form of carbon in iron. This is borne out by studies on the heat of formation of cementite,[4] which is found to have a negative value of some 13,600 calories per gram molecular weight of Fe_3C. This means that should 180 grams of Fe_3C decompose into iron and graphite, that much heat would be liberated. It is slightly less than the heat of freezing of water.

The fact that cementite does *not* decompose in ordinary steels and pure iron-carbon alloys is a condition of metastability due to causes that are as yet somewhat obscure. Certain elements, however, tend to overcome this metastability and allow the carbon to precipitate as graphite at appropriate equilibrium temperatures. Silicon is the most effective element of this kind, and in the case of gray cast iron, much of the graphite is formed at, or just above, the freezing temperature of the eutectic. This results in the graphite crystallizing as plates from the semi-molten iron and thus effectively breaking up the continuity of the matrix.

Nickel also tends to favor graphitization but not nearly as effectively as silicon. Carbide-forming elements (Chapter XIX), such as chromium or tungsten, inhibit graphitization.

Again, the rate of cooling has much to do with graphitization, and a rapidly cooled or chilled casting may not be graphitized, whereas the same material slowly cooled or cast in dry sand may graphitize completely.

Malleabilization of White Cast Iron

Graphitization continues below the freezing temperature, and if the cooling is slow enough, all the carbon of the austenite will precipitate as graphite by the time the eutectoid temperature (723°C) is passed. Graphite, precipitated from solid solution (austenite), is,

[4] "Heat of Formation of Cementite," by G. H. Brodie, W. H. Jennings, and Anson Hayes, *Trans. Am. Soc. Steel Treating*, 10, October, 1926.

however, much more constricted than that precipitated from the liquid. If graphite flakes are already present, the lower temperature precipitation will continue on these flakes; but a process is in use by which the graphite is *entirely* precipitated from solid solution. This results in nodular or spherical graphite particles (Figure 10.5) and is known as the malleableizing process.
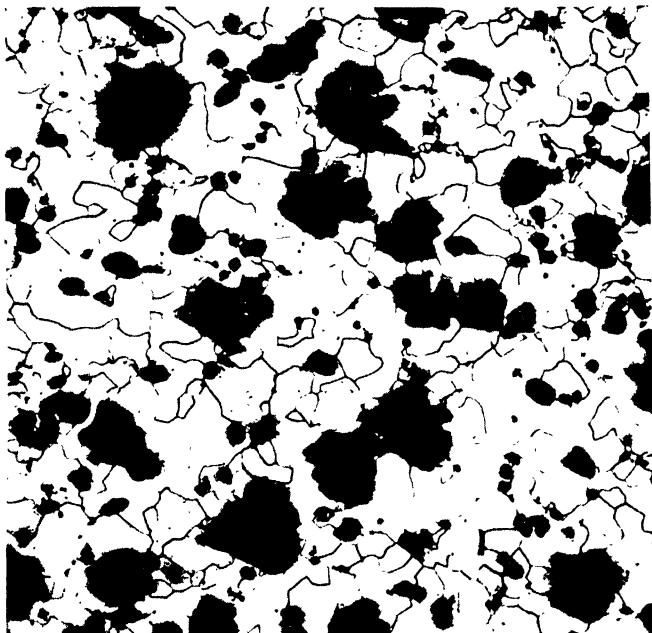
FIGURE 10.5. "Malleable," 100×.

The process consists in first producing castings of such silicon content that they will remain entirely white iron when cast in a green sand mold, but will become graphitized upon holding at a temperature in the neighborhood of 950°C. Such a material should analyze about as follows:

Carbon 2.50%
Silicon 90%
Manganese 1.50%

Residual alloys of chromium, tungsten, or molybdenum should be very low.

After cooling in the molds the castings are packed in boxes filled with sand and heated slowly to about 950°C. They are held at that temperature for several days and then allowed to cool very slowly past

the eutectoid temperature. After this they may be removed from the boxes and cooled in air.

The products of this treatment are completely graphitized castings composed of ferrite and nodular graphite. The graphite does not seriously break up the continuity of the ferrite matrix, and such castings are truly ductile. They are not malleable to the extent that they can be forged or rolled, but tensile tests will show considerable elongation
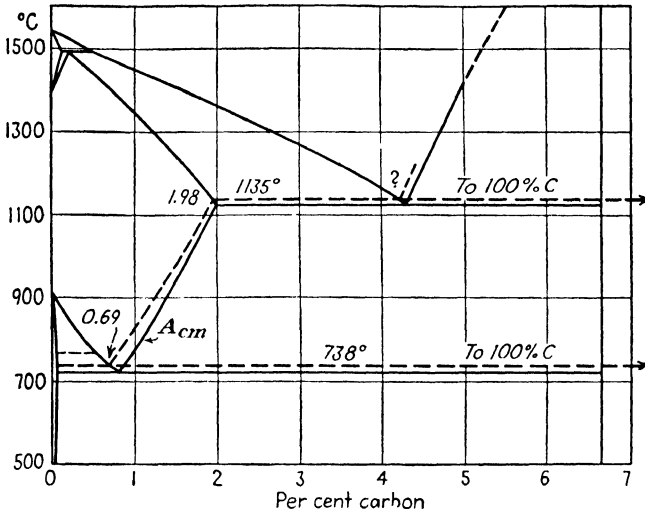
FIGURE 10.6. The stable and metastable iron-carbon equilibrium diagram. Stable lines ----, solutions in equilibrium with graphite; metastable lines ——, solutions in equilibrium with austenite, ferrite, or cementite. (Redrawn with modifications from *Metal Progress Data Sheets*, Am. Soc. Metals.)

and reduction of area, and bend test bars of one inch by one-half inch section can be bent through angles of forty-five degrees or more.

The superiority of such material over gray cast iron is obvious, and malleable castings enjoy great popularity in many fields of usefulness. They are, of course, more costly than gray iron castings but less costly than steel. They have excellent machinability and, because they can be cast into any conceivable shape, they can serve purposes for which forged steel is impracticable. They have extensive application in such automotive parts as housings, pedals, and control levers, and have even been used for engine crankshafts. Much household and domestic hardware such as hinges, lock parts, and handles is made from "malleable."

To date the best theory of the malleableizing process is based upon an assumed *stable* iron-carbon equilibrium diagram (Figure 10.6). In this diagram the dotted lines indicate the compositions and tempera-

tures of liquid or solid solutions that are in equilibrium with graphite instead of cementite. These lines lie above and to the left of the corresponding lines for equilibrium with cementite.

According to such a diagram, alloys that are cooled rapidly will be undercooled with respect to graphite. If the undercooling is slight and time be allowed, graphite will form slowly, but if the undercooling is so great as to bring the temperature below the metastable *Acm* line, cementite will form in preference to graphite. Continued cooling will preserve the cementite to lower temperatures and allow pearlite to form from the remaining austenite.

In the malleableizing process extremely slow cooling is necessary to prevent pearlite from forming in the eutectoid range. The *iron-graphite eutectoid* is somewhat conjectural. Because of the small amount of graphite involved (less than 0.7%) it is well-nigh impossible to demonstrate metallographically.

The Widmanstätten Structure

The structure of hypoeutectoid steels is usually described as consisting of "islands" of pearlite surrounded by a network of ferrite. This structure is generally characteristic of steels that have undergone at least one reheating into the austenite range of temperature. Steels in their original cast condition, particularly in large sections, show much larger, coarser, ferrite meshes. The pearlite islands are thus large, as were the austenite grains from which they transformed. It should be clear that each austenite grain results in one pearlite island. (Also see Chapter XIII.)

However, when the austenite grains are large there is not sufficient time, even with slow cooling, for the migration of the carbon necessary to concentrate all the proeutectoid ferrite at grain boundaries. Under these conditions, some ferrite will crystallize within the austenite grains. Such ferrite crystals will not be shapeless masses but will assume a form that is conditioned by the combined effects of their own atomic pattern (body-centered cubic) and that of the austenite grain (face-centered cubic) from which they grow. The form thus assumed is that of plates which are parallel to planes of closest atom packing in the austenite grain and also to planes of closest atom packing in the ferrite crystal. The planes of closest atom packing in the austenite grains are the $\{111\}$ or octahedral planes (Appendix I). Those in the ferrite crystal are the $\{110\}$ or dodecahedral planes.[5]

The ferrite plates thus formed produce a criss-cross pattern of the

[5] According to the mechanism of Kurdjumow and Sachs (*Z. Phys.*, 1930), in the transformation from gamma to beta iron or the reverse, a $\{111\}$ plane in the gamma phase is parallel to a $\{110\}$ plane in the beta phase, and a $[1\bar{1}0]$ direction in the gamma phase is parallel to a $[1\bar{1}1]$ direction in the beta phase.

massive ferrite within each pearlite island (Figure 10.7). There are four possible octahedral plane orientations in each austenite grain, so there will be a maximum of four plate directions in each pearlite island.

This structure was first observed in iron meteorites by Alois von Widmanstätten of the Vienna Porcelain Works in 1808. Although he
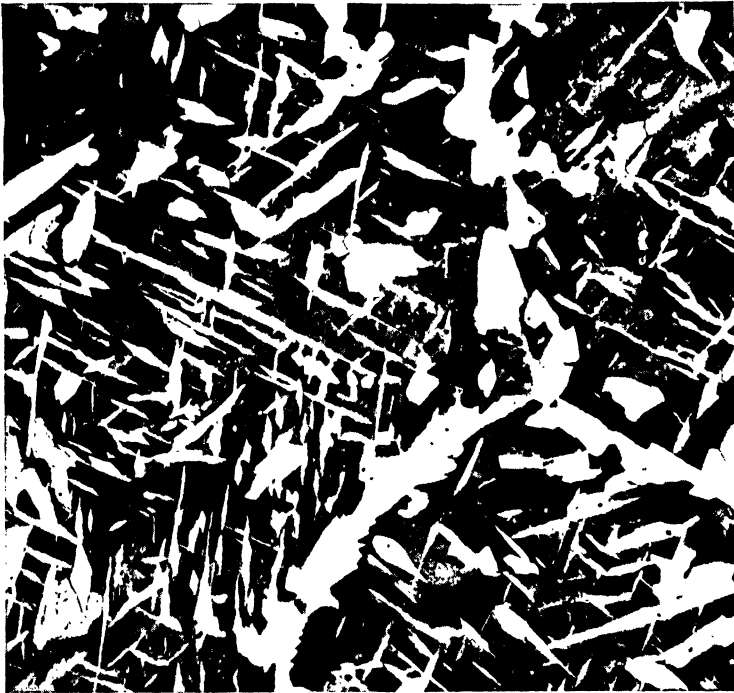
FIGURE 10.7. The Widmanstätten structure in cast steel, 100×.

apparently published no account of it, it was named for him by others who became interested in it. Recently it has been demonstrated by Mehl and others that mechanisms of a nature similar to that described for the transformation of iron operate whenever one crystal phase is formed from another, and the term Widmanstätten structure is applied generally to all alloy systems showing similar patterns.

Steel does not necessarily have to be in the form of castings to exhibit the Widmanstätten structure, as this will usually occur whenever the austenite grain is large. Thus, overheating of steel during annealing can produce large austenite grains, and the Widmanstätten structure will develop on cooling. In rolled or annealed steel it is considered as evidence of overheating.

QUESTIONS ON THE TEXT

1. Why should it be possible to forge or roll any true steel?

2. Are the cementite crystals in Figure 10.2B dendrites?

3. Of what are the dendrites of Figure 10.2A composed?

4. What is white cast iron? gray cast iron?

5. Of what phases does ledeburite consist?

6. What is meant by *graphitization?* What conditions or elements promote it?

7. What is "malleable"? Describe its structure.

8. What is a Widmanstätten structure? What conditions promote it in steel?

PROBLEMS

1. What are the per cents of ferrite and of cementite in pearlite containing 0.80% carbon?

2. A steel contains a total of 17% cementite. What is its carbon content?

3. Is the steel of Problem 2 hypoeutectoid or hypereutectoid? What is the per cent of pearlite and of the other structural feature?

4. Compare the per cents of pearlite and network material in the structures of a hypoeutectoid steel containing 0.80% − 0.20% (= 0.60% C) and a hypereutectoid steel containing 0.80% + 0.20% (= 1.00% C).

5. What will be the per cents of ledeburite and austenite in a white cast iron containing 3.50% carbon, at the eutectic temperature?

6. What will be the per cent of pearlite formed at the eutectoid temperature in the iron of Problem 5? What will be the per cent of ferrite?

7. What should be the per cents by weight of ferrite, graphite, and cementite in a gray cast iron that analyzes 3.8% total carbon and 0.5% combined carbon?

8. In the iron of Problem 7, if the density of ferrite is taken as 7.87 grams per cubic centimeter, that of cementite as 7.73 grams per cubic centimeter, and that of graphite as 2.22 grams per cubic centimeter, then what per cent of the microsection area should be graphite?

SUPPLEMENTARY QUESTIONS

1. What name is given to crystals that resemble the cementite crystals of Figure 10.2B in mineral aggregates?

2. What determines the coarseness of the ferrite network in a hypoeutectoid steel? How can this be varied?

3. Would you expect the most rapid change in physical properties with carbon content to be above 0.80% carbon or below?

4. Considering cost, ease of production, strength, and other physical properties, what kind of ferrous material discussed in Chapter X would you choose for each of the following applications: railroad rails, log chains, baling wire, engine cylinders, sash weights, automobile axles, leaf springs, car couplings, bathtubs?

Methods of Manufacture of Iron and Steel

The Blast-Furnace Process · The Manufacture of Steel · The Besse-mer Process · The Open-Hearth Process · The Crucible Proc-ess · Electric-Arc Processes · High-Frequency Induction · The Ingot Stage of Steel Manufacture

For a clear understanding of the properties and behavior of steel and iron it is essential to know something of the methods and principles involved in their manufacture, especially those phases of manufacture affecting the quality of the finished product.

The Blast-Furnace Process

All the successful large-scale production methods of manufacture of iron alloys start with the blast furnace. This is a large cylindrical stack, some 90 feet high and 15 to 20 feet in diameter at the widest part. Into it is charged iron ore, limestone, and coke. The charge enters the top of the furnace; preheated air is blown into the furnace near the bottom; and the heat developed by the combustion of some of the coke causes the ingredients to react together. The final results of the reactions are iron, slag (composed of mixtures of lime and aluminum silicates and other impurities), and gaseous oxides of carbon (CO_2 and CO).

The process is continuous, the reactions being completed as the metal settles down to the bottom, or hearth, of the furnace. The slag and metal are tapped out through holes located near the bottom. The metal is either run, molten, into large ladles to be taken directly, while still molten, to the steelmaking process, or is cast into horizontal

bars weighing from 50 to 200 pounds each, called *pigs*, which can be remelted as needed. Modern blast furnaces will produce from 600 to 1200 tons of pig iron every twenty-four hours.

In this process an excess of coke is always used so the metal, when it is tapped out, is practically saturated with carbon. Such highly *reducing* conditions, in addition to changing the iron oxide of the ore to iron and CO gas, are not without effect on other materials present. Considerable quantities of manganese are always present in the ore, and some of this is reduced. In fact, it is possible to make by blast furnace methods a high manganese-iron alloy for use in steel manufacture. Silicon, likewise, is reduced from SiO_2 in considerable amounts. Phosphorus remains as iron phosphide, dissolved in the iron. Sulphur, always present in both coke and ore, may be largely removed as calcium sulphide in the slag, if the lime charge is kept high. This is fortunate because the steelmaking processes are feeble removers of sulphur.

Pig Iron

The finished product of the blast furnace, namely pig iron, will analyze:

Carbon	3% to 4%
Manganese	0.5% to 2.5%
Silicon	1% to 2.5%
Phosphorus	0.2%
Sulphur .	less than 0.10%

The above is customary large-scale American practice. However, wide deviations from this practice and product can be found.

The Manufacture of Steel

Pig iron, a highly impure material, containing at least 5% of impurities, must be partially purified to be made into steel. As might be supposed, all the steelmaking processes depend upon *oxidation* for removal of impurities. The oxidized impurities, being non-metallic and of low density, float out of the metal and melt together forming a slag.

A great many methods of steelmaking have been devised. The oxidation is effected in various ways. It may be accomplished by pouring the liquid metal into a hollow, pear-shaped vessel, through holes in the bottom of which air is blown, thus causing the metal to be oxidized. This is the principle of the well-known Bessemer process.

The Bessemer Process

The Bessemer process serves to illustrate the manner in which oxidation purifies the pig iron and converts it into steel. The converter consists of a brick-lined shell supported on trunnions which allow it to swing around 360°. Air is led under pressure through one or both of

AIR   AIR
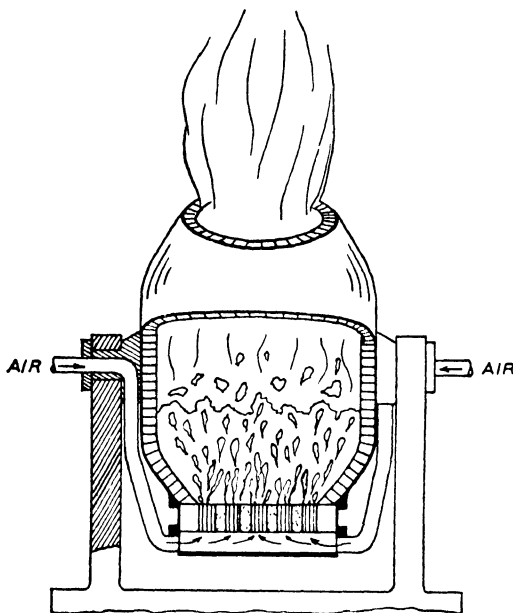
FIGURE 11.1.   Sectional view of Bessemer converter.

the trunnions, which are hollow, into a box at the bottom of the converter. From there it passes upward through small holes and bubbles through the molten metal. The shell is turned to a horizontal position to receive a charge of metal or to pour out the charge when the process is completed. The charge ranges in size from 1½ or 2 tons in small converters to 25 or more tons in the largest converters.

The process is very rapid, the time required to convert a single charge being from twelve to twenty minutes. During this time an interesting series of reactions takes place, and the nature of the reactions is seen in the appearance of the flame coming out of the mouth of the converter. This flame is due, in part, to the products of the reactions between the oxygen of the air and the constituents of the metal, and, in part, to the large volume of nitrogen which composes four-fifths of the air and which does not react with the metal but is heated to a high temperature in passing through it.

The Chemistry of the Bessemer Process

In the Bessemer process the oxygen combines with the metal as soon as it reaches it, presumably to form iron oxide at first. However, the iron holds the oxygen only long enough to pass it on to some constituent whose oxide is more stable at that temperature than FeO. Eventually the substance that forms the most stable oxide will receive the oxygen, and that oxide will either float out as slag or be carried out in the rush of gas.

When the blow is first started the silicon is the substance that forms the most stable oxide. Manganese follows a close second, and these are burned out first, the silicon completely, and the manganese less so. The flame, at this time, is a dull transparent yellow color and is filled with dusty looking sparks. This is known as the silicon flame and continues until the silicon is practically all removed from the metal. The sparks are largely SiO_2 which is carried out as small particles by the rush of gas.

The oxidation of the silicon produces a great deal of heat and causes the temperature of the melt to rise several hundreds of degrees. When the silicon is all burned out, the flame begins to look brighter and longer. Soon it becomes dazzling white and from 25 to 50 feet long. This is the carbon flame. The oxidation of the carbon in the metal produces CO, which, upon reaching the outside air, burns to CO_2. It is the most spectacular of metallurgical operations and at night, under low-hanging clouds, will sometimes give light enough to read by within a radius of 2 miles.

After the carbon is nearly all consumed, the iron itself begins to burn. This is indicated by a shortening of the carbon flame and the formation of billowy clouds of dark red smoke. This is the sign that the operation is complete, and the converter is turned on its side and the air blast is shut off.

While most of the manganese was oxidized along with the silicon, as noted above, a small percentage usually remains in the metal, even after the carbon is nearly all eliminated. At the finish of the blow the metal may analyze about as follows:

Carbon	0.06%
Manganese	0.10%
Phosphorus	0.10%
Sulphur	0.05%
Silicon	0.01%

The total is not much over 0.30% oxidizable impurities. A study of the laws of mass action and chemical equilibrium will indicate that under

these conditions it would require a considerable excess of oxygen to reduce the amount of the impurities much farther, and that, with this much carbon and manganese, there can be considerable FeO present with no reaction taking place. The FeO causes trouble because it reacts with the carbon as the metal freezes in the molds and forms CO, which causes the metal to become porous and spongy.

Deoxidizers

Therefore, as the metal is poured from the converter into a ladle, materials are added to deoxidize, that is, remove the excess FeO from the metal. These materials are some of those things that were burned out, namely, manganese and silicon. Even carbon may be added in the form of coke or, perhaps, molten pig iron, to bring the composition to some exact point. The metal is then ready to be transferred to the molds. Occasionally, as the metal is poured or *teemed* into the molds, aluminum is added as a further deoxidizer.

A list of deoxidizers in order of efficiency, or potency, puts aluminum first, then silicon, titanium, and manganese. The value of manganese is apparent from what has been said before. Silicon is used next in order to save on the more expensive aluminum. Titanium is sometimes used in place of silicon.

The Open-Hearth Process

In the past forty years the Bessemer process has given way, in large part, to the better controllable open-hearth process. In this process a large quantity of metal is melted or kept molten in a shallow basin made of refractory material by a flame which passes over the basin. The flame is produced by the union of preheated gas [1] and air, and the heat is reflected down onto the bath by a refractory roof over the furnace (Figure 11.2).
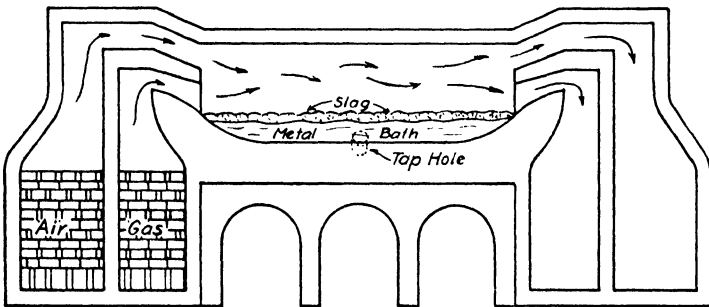

FIGURE 11.2.   Sectional view of an open-hearth furnace.

[1] Fuel oil, tar, or powdered coal may also be used.

At each end of the furnace are large chambers, loosely filled with brick, through which the hot gases pass on leaving the furnace at one end, and in which, at the other end of the furnace, the air and fuel gas are heated just before entering the combustion zone. The direction of flow of the gas is reversed every fifteen or twenty minutes so that the preheating chambers are kept freshly heated. This preheating process, known as "regeneration," is economical of fuel and secures an extremely high temperature.

The operation of the open-hearth furnace consists in charging the pig iron (either molten or cold), steel scrap, and limestone as a fluxing material to make the slag fusible. Instead of relying on the oxygen of the air to burn out the impurities, iron ore, consisting mostly of Fe_2O_3, is also charged. Heat is applied, and the scrap and cold pig iron are melted. The oxygen of the iron ore reacts with the silicon, manganese, and carbon in about the same order as in the Bessemer process, only more slowly, and the limestone is calcined and reacts with the silica and other oxidized impurities, forming a liquid slag which floats on top of the bath of steel.

When the metal is entirely molten and the reactions are complete, which is indicated by the bath becoming less agitated, deoxidizers are added and the metal is tapped out through a hole in the back of the furnace. It is caught in a large brick-lined ladle, and more deoxidizers are added in the same way as in the Bessemer process.

The open-hearth process requires from five to eight hours, but large modern furnaces may produce as much as 200 or more tons of steel in one heat. It utilizes lower grade ores and pig irons than can be worked satisfactorily in the Bessemer process and is generally considered to produce a better grade of steel than the Bessemer process because more time is allowed for reactions to complete themselves and for the products of these reactions to float out of the metal. In the case of the basic open-hearth process, which is the popular one in this country, phosphorus and some of the sulphur are removed from the metal along with other impurities.

The Crucible Process

The crucible process is another method of steelmaking. In recent years in the United States it has been supplanted by the electric processes. It is, however, of historical interest and the name "crucible steel" still persists.

The process is a small-scale production method of making extremely high-grade steels for tools and specialties. It consists, briefly, of melt-

ing charges of metal calculated to give exact compositions in crucibles made of graphite and clay. About 100 pounds of metal is melted in each crucible which must be handled manually with tongs.

Electric-Arc Processes

In the electric-arc processes the metal is melted in a bath, as in the open hearth, but the heat is supplied by means of electric arcs from carbon electrodes. These enter the furnace through the top and are kept close to the bath so that the arcs are between the electrodes and the metal. With three-phase circuits the metal acts as a Y connection. The power consumption is about 600 kilowatthours per ton of steel produced. The emf is usually between 100 and 200 volts.

The metallurgical operation of the electric furnace is quite similar to that of the open hearth except that closer control of quality and composition is maintained. The atmosphere above the bath is always reducing because of the presence of the electrodes. All oxidation is effected by means of the added ore, and elimination of residual oxygen is more nearly complete than in any other large-scale process.

High-Frequency Induction

Another electric process that has some commercial application in the manufacture of specialties, such as high-grade tool steel, is *high-frequency induction*. In this process an alternating current of several thousand cycles per second is passed through a water-cooled coil which surrounds the crucible containing the metal. Eddy currents are induced in the metal which, by virtue of its electrical resistance, becomes hot and melts. The high-frequency current may be generated by a high-frequency dynamo or by a resonant electric circuit involving large induction coils, condensers, and oscillatory spark discharges in chambers filled with inert gas, usually hydrogen.

The process can be made quite rapid and installations range from a few pounds to over 4 tons capacity. It yields results equal to, or surpassing the old crucible process and is amenable to every conceivable control. Melts can be made under selected atmospheres and vacuum melting has become a commercial possibility by this process.

The Ingot Stage of Steel Manufacture

Having surveyed in great haste the foremost methods of steel-making, we will follow the metal to the casting pit where, in sand molds, it may be cast into the final form of *steel castings,* or where it

may be cast into large masses known as *ingots,* which are later rolled or forged into useful shapes. The illustration, Figure 11.3, shows the manner in which the metal is transferred from the ladle to the ingot mold.
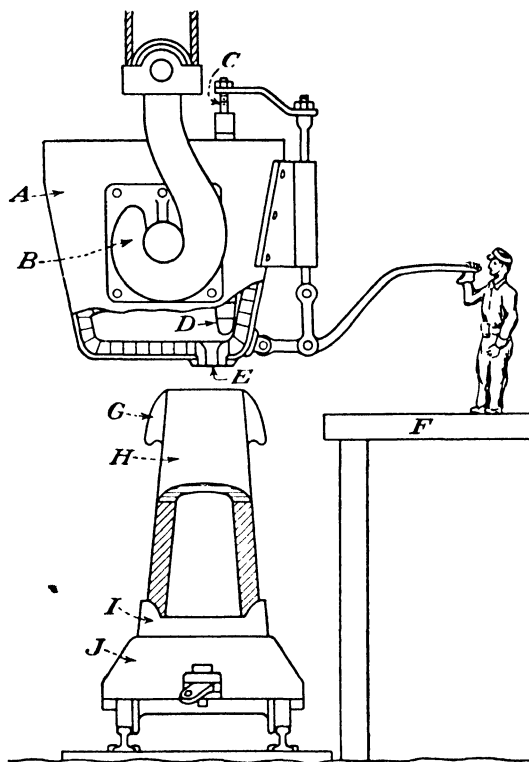
FIGURE 11.3. Pouring or teeming the ingot. (A) Ladle (steel shell lined with firebrick). (B) Crane hook. (C) Stopper rod. (D) Stopper head. (E) Nozzle. (F) Pouring platform. (G) Lug for removing mold from ingot. (H) Ingot mold (cast iron). (I) Stool. (J) Buggy.

Deoxidation and Rimming of Ingots

When first cast into the ingot mold, steel has a tendency to be "wild," that is, the gases liberated as it freezes cause it to froth or "boil," forming spongy cones of metal on the top and causing sponginess throughout the interior of the ingot. The formation of the cones is sometimes called bleeding. One method of overcoming this is to add aluminum to the molten metal as it is being teemed into the mold. This is said to kill the wild metal and cause it to freeze quietly. Steel so treated is called *killed steel.*

Another method consists in avoiding much deoxidizer (silicon or

aluminum) in the ladle and purposely keeping the steel hot and wild. Then, when teemed, it will set up a churning action due to the liberation of gases as it freezes. This brings the gases to the top surface and keeps that surface molten to permit the gases to escape quickly. This process is known as rimming, and steel made by it is known as *rimmed steel.*

After the metal has solidified, it is removed to the stripper where the mold is *stripped,* that is, removed from the ingot, by a specially designed crane. The ingot is next charged into the soaking pit, a sort of high temperature oven, where it is held at a temperature above 2000°F for a period of a few hours. This gives it opportunity to become uniform throughout in temperature. It is then passed to the rolling mill or forge plant where it is rolled into rails, plates, slabs, or bars, or forged into various shapes.

QUESTIONS ON THE TEXT

1. What materials enter a blast furnace and what materials come out of it?

2. What type of chemical reaction goes on in the blast furnace, and what type of reaction is essential to steelmaking?

3. What impurities are removed in the Bessemer converter and in what order?

4. What are meant by deoxidizers? When and why are they used?

5. List the reasons why the open-hearth process is the most used steelmaking process.

6. What are *rimmed ingots?*

SUPPLEMENTARY QUESTIONS AND PROBLEMS

1. What useful material other than pig iron is produced in the blast furnace?

2. If the density of pig iron is 7 grams per cubic centimeter what is the volume of the 1200 tons of pig iron produced in 24 hours by a modern blast furnace?

3. If iron and its impurities are burned by air and cause the temperature to rise in the Bessemer process, why is not iron burned when heated ordinarily? Or is it burned?

4. If at the end of the blow the Bessemer metal analyzes as shown on page 102, and if it is desired to bring the carbon up to 0.30% (assuming no loss), how much pig iron of the following analysis should be added to a 25-ton heat: C, 3.5%; Mn, 1.5%; Si, 1.5%?

5. If 20% of the added manganese in Problem 4 is lost by oxidation, what will the resulting manganese content of the steel be, and how much ferromanganese containing 80% Mn must be added to bring the manganese content up to 0.50%?

6. How much silicon is introduced by the added pig iron in Problem 4, and if it is all oxidized, how many per cent of oxygen[2] in the original 25 tons of steel should it account for?

7. What factors limit the temperature to which a regenerative open hearth furnace can be heated?

[2] For solubility of oxygen in liquid iron see "Evolution of the Iron-Oxygen Constitutional Diagram," by C. H. Mathewson, E. Spire, and W. E. Milligan, *Trans. Am. Soc. Steel Treating,* **19,** Nov., 1931, p. 68.

Defects and Impurities in Steel

The Finishing of Molten Steel · Defects in Steel · Impurities in Steel

The Finishing of Molten Steel

We have seen that at the finish of the melting process there is an approximate balance between the state of oxidation of the metal and the composition, particularly as regards the carbon. When the carbon drops below 0.20%, as frequently happens in standard practice, the reaction with oxygen becomes slower, and under certain conditions a considerable amount of oxygen, as iron oxide, may remain suspended or dissolved in the molten metal, even in the presence of a few hundredths of a per cent of carbon. However, the effect of the presence of the oxide in the molten steel is to react slowly with the carbon to form carbon monoxide (CO). The steel becomes saturated with this, even supersaturated, until it freezes in the mold. When freezing occurs the carbon monoxide, being insoluble in solid steel, is liberated as a gas and forms bubbles in the partly solidified ingot. This condition is avoided by the addition of metallic aluminum to the steel as it pours into the mold. The aluminum reacts instantaneously with the oxygen of the iron oxide and of the CO to form alumina (Al_2O_3). However, if the original amount of iron oxide was large, the ingot is finally left with a large amount of Al_2O_3 distributed as extremely fine particles throughout the steel. In many cases this is not desirable, and the attempt is made to minimize the residual oxygen by slow careful work in completing reactions in the furnace. Another alternative is the use of the rimming process, which is referred to in the preceding chapter.

Another bad effect of overoxidation of the metal is the formation of particles of iron oxide itself, which may form in the ingot as a

result of lowered solubility when the ingot freezes. This is one of the sources of "sonims" (solid non-metallic included materials).

Defects in Steel

Blowholes

Gaseous voids, as described above, may easily occur and are called blowholes (Figure 12.1). They are present to a certain extent in all ingots and, if deep seated so that their interiors do not become oxidized, they are squeezed out and largely eliminated by their surfaces welding together in the rolling mill. When they are near the surface of the ingot, however, they may become oxidized so that they cannot weld. They will then cause cracks to form in the side of the ingot as it is rolled. These cracks are stretched out by subsequent passes through the rolls and form *seams* in the finished bars. They are very detrimental to plates, sheets, wires, and forging stock that has to undergo upsetting operations, that is, be compressed in the direction of its length.
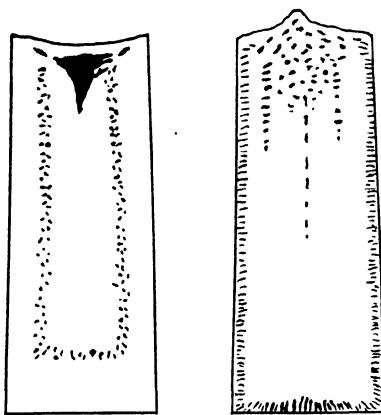
FIGURE 12.1. The effects of blowholes. Left, deep-seated blowholes, harmless; right, surface blowholes, objectionable.

Scabs and Cold Shuts in Ingots

As the metal is poured from the ladle into the ingot mold it frequently splashes on the side of the mold, some of it freezing instantly, forming a thin sheet. As the mold fills up, this sheet attaches itself to the ingot in a loose manner, most of the surface remaining separated by a layer of oxide. It then becomes a scab on the surface of the ingot, breaks into pieces during the rolling, and thus ruins the surface of the finished bar. The scabs formed in this way are sometimes called cold shuts.

The term "cold shut" is, however, more accurately applied to a defect arising from the shrinking of the metal that normally solidifies against the wall of the mold. This shrinkage causes the solidified metal shell to pull inward from the mold wall and allow more molten metal to overflow it, forming a fold. Cold shut is the term applied to the fold. Its effect is quite similar to that of scabs.

Pipe in Ingots

Since solid steel has a greater density than molten steel, it shrinks as it freezes. The outside of the ingot freezes first, of course, and becomes a mold for the inside. The outside, having frozen, does not shrink much more, but the molten metal inside continues to freeze and shrink, leaving a large void in the upper portion of the ingot. The sketches in Figure 12.2 illustrate this manner of freezing and shrinking.
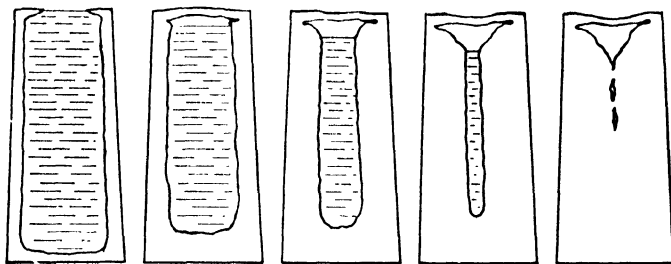

FIGURE 12.2. The formation of pipe.

This void or cavity is called *pipe* and is very detrimental to sheets, plates, slabs, rails, and in fact most sections rolled from killed [1] steel ingots. The void may be eliminated by discarding the upper portion of the ingot, and although this is very wasteful, it is the commonly used method. Pipe is absent in rimmed ingots, but rimming is often not suitable for the type of steel being produced.

Another way to minimize the effect of pipe is to cast the ingot with the big end up and have a refractory tile on the top of the mold. The inverted mold allows solidification to proceed to a greater extent from the bottom upward, and the refractory tile, known as a *hot-top*, supplies a reservoir of molten metal that fills up the pipe cavity as it forms. Special methods must be used to strip the inverted mold from the ingot and these entail considerably increased cost.

Pipe is minimized in ordinary ingots by the judicious utilization of blowholes. By controlling the amount of deoxidizer that is added to the ingot, a limited amount of gas is allowed to form in the interior. This counteracts the piping tendency and the blowholes and sponginess are eradicated in the rolling.

Segregation

If we remember the liquidus and solidus of the equilibrium diagram, we will recall that the first portion of the metal to freeze was purer

[1] See page 106.

than the liquid. This results in a progressive variation in composition of the solid phase, from the first portion to freeze to the last, the last portion to freeze being the least pure. This will generally be at the center of the upper portion of the ingot. Naturally, the variation in composition is very undesirable especially where uniformity of quality and physical properties is essential. Steel in this condition is said to be *positively segregated.*

Another kind of segregation, known as *negative segregation,* often occurs in the lower part of the ingot. This is due to the formation, as freezing progresses, of loose crystals of solidified metal which settle to the bottom of the liquid. These crystals are normally purer than the liquid from which they form and yet are collected in the deep interior of the ingot with the result that the central portion is of greater purity than the metal which surrounds it.

The best remedy for segregation seems to be the formation of dendritic crystal growths. These distribute the first and last portions to freeze in such a way that there is no general gradient in composition from center to outside of the ingot, but rather from center to outside of each dendritic branch. Thus the less pure and the purer portions are all mixed. During the time the ingot is kept hot in the soaking pit, and especially when the steel is heat-treated after rolling, the differences will be largely eradicated by diffusion.

In rimmed steel it is not possible to secure such well-developed dendritic growths, and the rimming or churning action of the metal continually sweeps the less pure metal out of the dendrite cavities and concentrates it in the center of the ingot. For this reason rimmed steel has a tendency to segregate badly.

Ingotism

Dendritic growths are not without their bad effect, however. As the ingot starts to freeze against the cold wall of the mold, crystal dendrites start to grow at a large number of places on the surface. These quickly meet at grain boundaries when they grow parallel to the wall of the mold, but they continue to grow toward the center of the ingot.[2] This results in long grains from outside to center of the ingot. If the metal contains much non-metallic included matter or embrittling impurities like sulphur or phosphorus, this will give rise to an intercrystalline brittleness that causes the crystals to break apart as the metal is squeezed through the rolling-mill rolls, forming bad seams and tears and sometimes literally breaking the ingot in two. Correct furnace practice and correct pouring or casting temperatures are aids in controlling this condition, for which the term "ingotism" has been

[2] See Figure 24.1 for an example of ingotism in copper.

coined. For special steels of high quality, a circular corrugated mold is sometimes used. By this the direction of the crystals is such that they soon run into each other and the single-crystal tendency is broken up.

The five conditions just discussed, namely, blowholes, scabs, pipe, segregation and ingotism, comprise the common defects that occur in the ingot stage of manufacture. They are common to all metals that are cast in ingots, including copper, nickel, Monel, brass, bronze, aluminum alloys, and many others. Steels that are to be used for structural purposes can sometimes be allowed some of these defects if not too prominent, but forging steels, tool steels, steels to be heat-treated, and steels that have to withstand dynamic loading, such as repeated or reversed stresses, must be practically free from such defects.

Impurities in Steel

It is customary to classify the carbon steels as if they were binary alloys of iron and carbon, and yet it must be admitted that, in all commercial steels, other elements are present in very considerable amounts. Some of these elements are merely impurities of an undesirable nature

FIGURE 12.3. Corrugated mold for inverted ingot. (Drawn to scale from sketches in "Basic Open-Hearth Steel Making," Am. Inst. Mining Met. Engrs.)

which have been reduced in amount until their effects can be tolerated. Others are present because they have been used to produce certain chemical reactions in the manufacture of the steel. Some are used to produce mild variations in the quality or properties of the metal, but are not used in sufficient quantity to allow the metal to be classified as an alloy steel.

A list of these elements includes manganese, silicon, copper, nickel, phosphorus, sulphur, aluminum as aluminum oxide, oxygen, and occasionally tin. The usual steel plant analysis of carbon steels lists carbon, manganese, phosphorus, sulphur, and silicon, where no other element is intentionally added.

It is well to understand the specific effects of these elements because often some of the unusual characteristics and elusive defects that occur occasionally in steel articles are traceable to an excess or deficiency in some of these usual impurities.
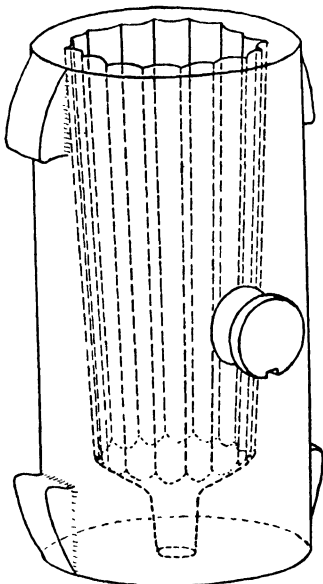
Manganese heads the list because it is present in the largest amount and affects the alloy in a manner that is second only to that of carbon. It is an essential ingredient from the standpoint of the steel manufacturer. An interesting digression into the history of steelmaking illustrates and explains the importance of manganese.

Origin of the Bessemer Process

The first large-scale production method of steelmaking that was developed was the Bessemer process. As described in the preceding chapter, this process consists, simply enough, in bubbling air through molten pig iron, or blast furnace metal, in a cylindrical vessel called a converter until the carbon and other impurities have been burned out of the metal. The idea was first worked upon by William Kelly of this country, a practical iron manufacturer with an inventive turn of mind. His chief difficulty lay in the fact that the metal was so charged with gas and oxygen at the end of the blow, that when it was poured into molds the gas that was liberated as the metal started to freeze caused the casting and ingot to be extremely spongy or porous and to froth out of the top of the mold. Not until Robert Mushet discovered that manganese added to the metal just before casting would reduce the gas content (by combining with the oxygen and therefore preventing the formation of CO) and so allow the metal to solidify quietly as a solid mass, was much progress made. Sir Henry Bessemer, of England, had been working on the same idea and obtained his patents ahead of Kelly, although both men were probably indebted to Mushet for the real solution to the problem.

The deoxidizing effect of manganese is an important quality. Other effects, however, help to make it indispensable in commercial steels. It controls the deleterious element, sulphur, in a peculiar manner. Sulphur, in pure iron, exists as iron sulphide. This is a hard brittle substance, somewhat soluble in molten iron. It forms as films between the grains of iron after the iron is solid. The effect of manganese is to change the iron sulphide to manganese sulphide which, being insoluble in the molten iron, forms rounded globules, some of which float out of the liquid metal; but those that remain in the metal do little actual damage.

A third effect of manganese is to control the structure of the steel. For some not easily explained reason, the development of well-formed, laminated pearlite is helped by the presence of manganese. This is an advantage in forging steels and steels that are to be heat-treated, but not always so in sheets. Sheets are often made of steels in which the manganese content is quite low.

The normal manganese content for structural steels, forging steels, plates, rods, wire, rivets, springs, railroad steels (other than rails), such as axles, frames, tie plate, many casting steels, and others is between 0.3% and 0.5%. Ingot iron has less than 0.1%, and rails usually require from 0.6% to 0.8%.

Even very small amounts of impurities have big effects on the electrical and magnetic properties, but manganese, in the amounts given above, has very little effect on the tensile properties. Above 1%, however, the effect of manganese on tensile properties is greater, but this will be discussed under alloy steels.

Silicon, like manganese, is added intentionally to steel as a deoxidizer. In some respects it is more effective than manganese in removing gases, and for this reason there is less residual silicon in the metal after it is cast. As far as the silicon itself is concerned, it does not have the other beneficial effects of the manganese. It is of no help in controlling phosphorus or sulphur and, in fact, the product of oxidation of the silicon (SiO_2), if added in a basic furnace, causes the phosphorus and sulphur to be reduced out of the slag by the iron.

At the end of the steelmaking process the manganese is usually added first, some perhaps in the furnace, and some in the ladle while the steel is being tapped. Silicon is added in the ladle.

Such silicon as remains in the metal is usually in the oxidized form (SiO_2) and is combined with other oxides and sulphides, such as MnO, FeO, MnS, and FeS, to form silicates and silicate glass. These appear in the microsection as rounded globules, non-metallic, and gray or tan in color. They are usually vitreous (non-crystalline) in character, and form the familiar *stringers* seen in longitudinal sections of rolled steel.

Silicon will vary from 0.01% to 0.30% in commercial steels. Such amounts do not appear to affect the tensile properties.

Copper and *nickel* may be classified together as regards their effects on carbon steels. They both find their way into the steel through the reclamation of scrap. With the increasing use of alloy steels containing nickel or copper it is evident that the average percentage of these elements is gradually increasing in the commercial steel scrap because the steelmaking processes have no effect in removing them. Most other alloying elements are almost entirely lost by the time the scrap is remelted. A small amount of copper gets into the steel through natural sources such as the iron ores used.

For most purposes neither the copper nor the nickel, in the quantities found in carbon steels, has any noticeable effect on the tensile properties. Nickel is quite soluble in solid solution in both ferrite and austenite. Copper is soluble in austenite but forms a precipitate in

ferrite. It is said that some high-carbon tool steels are adversely affected by the presence of relatively small amounts of copper.

Commercial carbon steels contain something less than 0.10% of either nickel or copper. As much as 0.50% copper is sometimes added to sheet steel. In this amount it is said to increase resistance to corrosion.

The role of *phosphorus* in steel is somewhat complex. Where it exceeds 0.10% it appears to produce brittleness, provided the carbon exceeds 0.15%. It occurs as a constant percentage in iron ores. The ratio of phosphorus in the Lake Superior ores is about 1 to 500 (0.2%), so that some of it must be removed in the steelmaking process. The basic open-hearth process accomplishes this, and specifications usually require less than 0.04% phosphorus in the finished steel.

Banding in Steel

Phosphorus in steel forms iron phosphide (Fe_3P) which is to a certain extent soluble in the ferrite and austenite. Its worst effect is that it diffuses very slowly through the steel at heat-treating temperatures. Its presence in streaks or bands in rolled or forged steel, due to dendritic segregation (see Chapter VII), is indicated by a distribution of the ferrite and pearlite areas in similar bands (Figure 12.4).

This *banding* is not eliminated by repeated annealing and was formerly explained on the theory that the segregated phosphorus [3] prevented carbon diffusion. However, this has been shown to be erroneous, and it is found that the same steel, quenched from a high temperature, will not show the banding. Moreover, annealing after this treatment will cause the banding to reappear. The probable explanation is that the high-phosphorus regions promote the early precipitation of ferrite on cooling from annealing temperatures. This results in a repetition of the banded structure even though the carbon becomes uniformly distributed each time in the austenite.

Phosphorus is added in amounts up to 0.20% to steel that is to be rolled through hand mills into sheets. In such mills the thinner sheets are doubled up and two or more are rolled at once. Under these conditions the phosphorus prevents them from sticking together.

Sulphur like phosphorus may not be tolerated in most steels in amounts exceeding 0.05%. Sulphur in higher percentages has a tendency to cause brittleness at high temperatures and if present as FeS causes the ingots to break up in the rolling mill. In all commercial

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[3] That phosphorus is not the only cause of banding is shown by the fact that some of the alloy steels show it in the absence of significant percentages of phosphorus.

specifications the manganese is placed high enough to convert all the sulphur to manganese sulphide. In this form it does little harm to the tensile properties of the steel.

In the case of one particular kind of steel, sulphur is intentionally added to the metal. This is for material like screw and bolt stock that
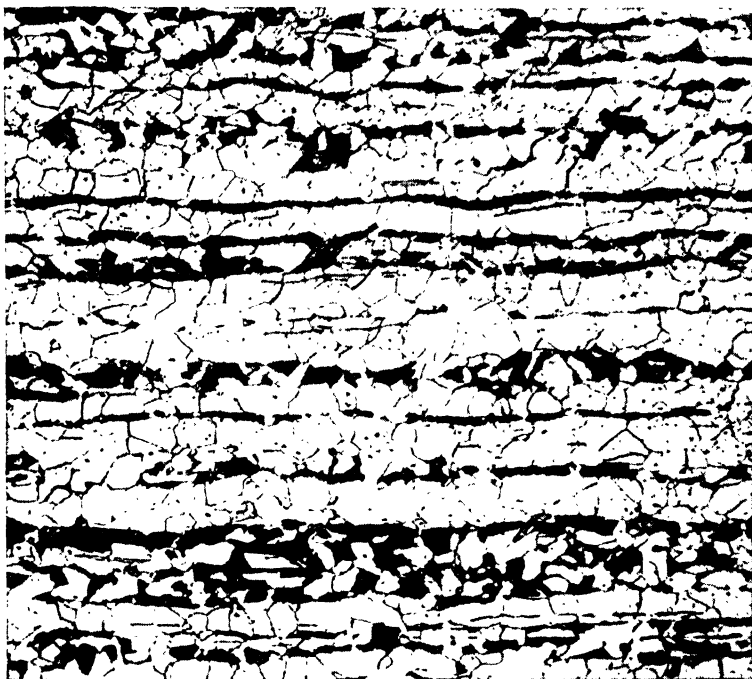

FIGURE 12.4. Banding in annealed mild steel (100×).

is to be extensively machined or threaded, and yet must be of low-carbon soft metal. Here the sulphur as manganese sulphide particles serves to break up the continuity of the metal so that the threading or cutting tool can cut out chips instead of plowing through the soft ferrite. The chips break up in such a way that higher cutting speeds can be used and there is less wear on tools.

Aluminum is often used as a deoxidizing agent in the last stages of steel manufacture and is usually added just as the steel is being poured into the mold. The aluminum is added in quantities that are entirely consumed by oxidation so that ordinarily no aluminum metal is left in the steel. A small amount of aluminum oxide in extremely finely divided form is thought to be left entrapped in the metal. Just what harm this does is not definitely known. It undoubtedly helps to con-

trol grain size. It is possible that it has an influence in promoting a tendency to fail by fatigue (see Chapter XV).

A better explanation of the deleterious effect of aluminum lies in its effect on the size and distribution of other non-metallic inclusions. According to work of Sims and Dahle and others, as quoted by Briggs,[4] as the aluminum addition approaches the exact amount necessary to react with all the oxygen, the solubility of the manganese sulphide increases greatly. This forms an intergranular eutectic when the steel solidifies, which so breaks up the continuity of the metal that the steel loses strength and ductility and has low impact strength. With lower or higher percentages of aluminum the sulphides are distributed more at random and do less harm.

Oxygen is, itself, a detrimental substance in steel. It is soluble in molten iron as dissolved iron oxide to the extent of 0.05% or more, but its solubility does not exceed 0.005% in solid iron. As in the case of sulphur, the iron oxide tends to form a film between the grains of iron and, in the absence of manganese, causes embrittlement and weakness. In steels containing normal amounts of manganese, however, this effect is greatly reduced.

Since the analysis of steel for oxygen is quite difficult and rarely performed, it is customary for users of steel to attribute unusual and difficultly explained defects to oxygen in the metal. This is an over-worked explanation, however.

Recent studies[5] have made a strong case for the effect of *hydrogen* in producing many of these defects. Heretofore unexplained weaknesses, such as intercrystalline brittleness in sheet steel, are nicely explained by the theory advanced by Zappfe and Sims that hydrogen may dissolve in iron at certain temperatures as monatomic hydrogen (H). This diffuses out of the iron at lower temperatures forming the insoluble H_2 as soon as it escapes from the metal solution. H_2 may thus collect in voids and submicroscopic fissures to build up tremendous pressures, which partly overcome the cohesive properties of the metal itself, causing it to be brittle and weak.

In addition to the impurities discussed above, there are a variety of non-metallic substances that become entrapped in the steel just before and when it freezes. Sources of these may be pieces of ladle refractory, droplets of slag, or the products of deoxidizing reactions. They appear in the microsection as small gray or black specks, usually

[4] *The Metallurgy of Steel Castings*, by C. W. Briggs, Chapter III, pp. 127–157, McGraw-Hill Book Co.

[5] "Hydrogen Embrittlement, Internal Stress, and Defects in Steel," by C. A. Zappfe and C. E. Sims, *Trans. Am. Inst. Mining Met. Engrs.*, 145, 225 (1941).

round or elliptical. They have been dubbed *sonims,* which stands for the words "solid, non-metallic, included materials." Their effect on the properties of the metal is doubtful. If present in very large numbers and amount they undoubtedly reduce ductility and tend to lower impact resistance, but extensive studies and counts have failed to show a correlation between mechanical properties and the amounts of these sonims encountered in ordinary commercial steels.

QUESTIONS ON THE TEXT

1. What is the purpose of adding metallic aluminum to steel? At what stage of the process is it usually added?

2. Are blowholes always detrimental to steel? Explain.

3. Describe three ways of dealing with pipe in ingots.

4. How may segregation be reduced in extent?

5. What are the purposes of (a) hot tops; (b) inverted molds; (c) corrugated molds?

6. What discovery made the Bessemer process possible?

7. Describe three beneficial effects of manganese in carbon steels.

8. What is meant by "stringers" in the microsection of steel?

9. How do copper and nickel get into carbon steels?

10. What is banding? What is one cause of it?

11. Have sulphur and phosphorus any uses in steel?

12. Under what conditions is aluminum most detrimental to steel?

13. What is hydrogen embrittlement and how is it explained?

SUPPLEMENTARY QUESTIONS AND PROBLEMS

1. If a 200-ton heat of steel contains 0.05% oxygen at the time of pouring, how much aluminum will be required to just react with this oxygen?

2. Name three gases other than carbon monoxide that might contribute to blowholes in steel.

3. Which ingot defects might contribute to bad surfaces in finished steel? Which produce bad interiors? And which may affect both surface and interior?

4. Should the embrittling effect of ingotism be greater with large or with small crystals? Why?

CHAPTER XIII

The Thermal Critical Points of Steel – the Heat Treatment of Steel

Recalescence Temperature and the Critical Range · Thermal Hysteresis · Essential Operations of Heat Treatment · Mechanical Properties Resulting from Heat Treatment · Definitions

We have already noted that property of steel whereby it is hardened by sudden cooling from a high temperature.[1] This fact alone would brand steel as an unusual substance and give it a variety of uses. But of equal importance is the fact that the actual hardness obtained can be regulated, either by controlling the rate of cooling or by reheating to some moderate temperature the piece that has been made as hard as possible. These two operations, hardening and reheating, comprise the essential steps in the process known as heat treating.

Recalescence Temperature and the Critical Range

In order to obtain a clear understanding of the principles of heat treating it will be necessary to become more thoroughly acquainted with the reactions and changes that take place when steel is heated and cooled through the range of temperature lying between 723°C and 910°C. This is called the critical range, the transformation range, and, loosely with reference to the reaction at 723°, the recalescence temperature. Because true recalescence, meaning reheating, is only possible as a result of supercooling below 723°C, it is evident that there is no scientifically exact point that corresponds to it.

[1] See Chapter VIII, page 73.

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If we reconsider that portion of the iron-carbon equilibrium diagram that has to do with steels in the critical range, Figure 13.1, we can visualize the changes that take place.

The sloping line *ace* is a boundary of the area that represents the composition and temperature of solid solutions of carbon in gamma iron, that is, austenite. It is likewise the solvus that represents compo-
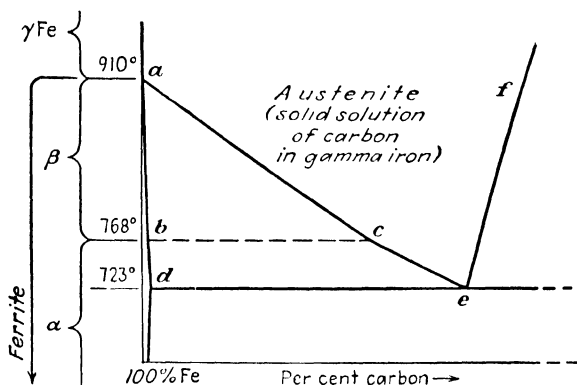

FIGURE 13.1. Iron-carbon equilibrium in the critical range.

sitions and temperatures of the austenite from which ferrite will crystallize on cooling. The line *ef* is the solvus that represents compositions and temperatures of austenite from which cementite (Fe_3C) will crystallize on cooling. The line *bc* represents the temperature at which ferrite becomes magnetic on cooling, and the line *de* represents the eutectoid temperature.

Theoretically, the reverse changes should take place on heating. The line *de* represents the temperature at which pearlite changes to austenite on heating. The line *bc* represents the temperature at which ferrite loses its magnetism, and the line *ace* represents the composition and temperature of alloys in which the last traces of ferrite have become dissolved into solid solution in gamma iron on heating.

Thermal Hysteresis

Practically, there is always a discrepancy between the temperatures at which these changes occur on cooling and the temperatures at which the reverse changes take place on heating. This discrepancy is due, in part, to the fact that time must be allowed for the changes to complete themselves and, in part, to tendencies to undercool or superheat. Such behavior is discussed in Chapter VII. As a result, even with very slow continuous cooling or heating, there remains a gap

between the temperature at which any particular change takes place on heating and on cooling. This gap is referred to as thermal hysteresis. It is quite similar in character to magnetic hysteresis although not in any way related to it.
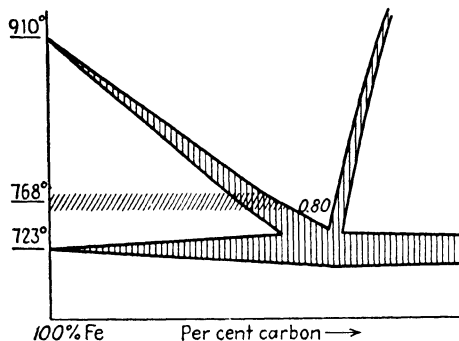
Although these conditions are not strictly speaking matters of equilibrium, they can be expressed in terms of composition and temperature and so may be plotted as lines on the equilibrium diagram. Thus, the location and extent of the hysteresis gap is indicated by the shaded areas on the diagram, Figure 13.2.

FIGURE 13.2.   Thermal hysteresis.

Symbols for the Transformation Temperatures

Of course, the lower portion in each case represents the temperature of transformation on cooling, and the upper portion represents the corresponding temperature on heating. For convenience in discussion, a system of nomenclature has been adopted generally by which all the lines in the transformation range may be verbally identified: (1) Any of the lines that have to do with the transformation are referred to by the letter A which is the initial of the French word *arrêt*, meaning arrest or halt, thus referring directly to the time-temperature cooling characteristic. (2) Subscript numerals are used to indicate the particular transformation referred to, that is, A_1 represents the line *dc*; A_2 represents the line *bc*;[2] A_3 represents the line *ace*; A_{cm} is sometimes used to represent the line *ef*. (3) An additional subscript r (from the French word *refroidissement*) indicates the transformation on cooling, and c (from the French *chauffage*) indicates the transformation temperature on heating. These are shown in Figure 13.3. In eutectoid steels, heated and cooled with reasonable slowness, the difference between Ar_1 and Ac_1 will be from 25° to 50°C.

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[2] Since the magnetic change takes place entirely within the ferrite, it is inconceivable that it should be affected by the carbon content where that exceeds the 0.025% necessary to saturate the ferrite. Thus there should be no hysteresis for the A_2 line. However, the heat effect at A_2 is very slight and somewhat difficult to detect and accurately locate. As the carbon content of the steel increases, the proportion of ferrite decreases and with it the accuracy of the determination of the A_2 point. This is probably one reason that early writers assumed that it showed hysteresis effects like A_1 and A_3.

Let us note, in passing, that the Ac and Ar lines meet at a point at the left of the diagram. This indicates that for pure iron there is no hysteresis gap. Although this is not strictly correct, it is true that un-dercooling is very much less in pure iron than in the iron-carbon alloys. This accounts in part for the fact that pure iron does not greatly respond to or change its properties with heat treatment.

In addition to the above nomenclature we may occasionally refer to the A_3 position as the upper critical temperature and to the A_1 position as the lower critical temperature.
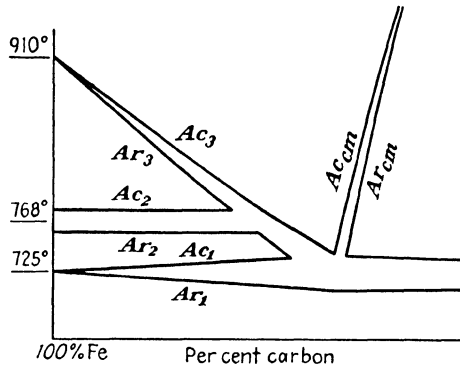

FIGURE 13.3. Nomenclature of the critical points.

Essential Operations of Heat Treatment

The essential operations in the heat treatment of steel are those already mentioned, namely, the hardening operation and the reheating after hardening to reduce the hardness a desired amount. The latter is known as tempering or drawing. Several other operations, however, are considered in the category of heat treatment. Some of these are independent of, and have other purposes than the two mentioned. Others condition, or prepare, the metal for the hardening and tempering operation.

Normalizing

This consists in heating a piece of steel to about 100°F above the upper critical temperature and cooling in air. It is usually a condition-ing operation prior to hardening. Normalizing relieves rolling strains, reduces grain size, and produces a finer structure. The discussion of the annealing process explains the mechanism of grain refinement.

Homogenizing

One of the effects of normalizing is to produce a more uniform com-position. This is known as homogenizing, or making homogeneous. We recall from Chapter XII that steel that is cast into ingots is likely to be segregated. If the segregation is general, that is, from outside to center, not much can be done about it, but a preventive suggested was the growth of dendrites in the freezing of the ingot. These may

be segregated in themselves but their intricate shape causes the pure and impure regions to be very much intertwined in the ingot as a whole. When the ingot is rolled out as a bar the pure and impure portions are stretched out into a bundle of very thin fibers or streaks. It is easy to see that the time required in the normalizing process, at the high temperature, might allow diffusion to proceed far enough to eradicate such very local variations in composition.

When normalizing is used as a homogenizing treatment a higher temperature may be employed to hasten diffusion.

Annealing and Grain Refinement

Annealing means softening by heat. *Full annealing* consists in heating a piece of steel to some temperature above its upper critical temperature (Ar_3) and cooling very slowly, usually with the furnace. Whenever a piece of steel is heated or cooled through its transformation range it undergoes complete recrystallization. Consider a piece of steel containing about 0.50% carbon and heated to above Ac_3 (perhaps 900°C). It will, at that temperature, consist entirely of the solid solution of carbon in gamma iron (austenite). When it is cooled to the upper critical temperature, Ar_3, which will be about 800°C, crystals of ferrite (body-centered iron) will begin to form at the boundaries of the face-centered austenite grains. By the time it has cooled to Ar_1 (below 723°C), the grain boundaries of the austenite have been replaced by a network of ferrite, and the residual, unchanged austenite, contains 0.80% carbon. Further cooling causes this residual austenite to decompose into the finely laminated mixture of ferrite and cementite, viz., pearlite. In each island of pearlite there will probably be several patches of pearlite of different origin and lamination direction.

If, now, we reheat the steel, when Ac_1 (above 723°C) is reached, the cementite and ferrite of the pearlite will redissolve in each other, forming the austenite solid solution. Presumably, this process will start independently at several points in each pearlite island, resulting in several austenite grains where originally there was one. As heating continues, the ferrite network dissolves in the austenite. When the upper critical temperature Ac_3 (above 800°C) is reached, no ferrite is left, but there are now more austenite grains than there were originally. The grain size must therefore be smaller.

If the process of cooling and heating were repeated, we might expect to get a still smaller set of grains, but this will not happen, or at least not go on indefinitely, for several reasons.

In the first place, after the austenite grains have become quite small

and the resulting pearlite islands are quite small, there is not much chance that more than one new austenite grain will develop in each pearlite island.

In the second place, another interesting and important factor comes into play which overcomes further grain refinement by annealing. This is the phenomenon of grain growth. The higher the temperature,
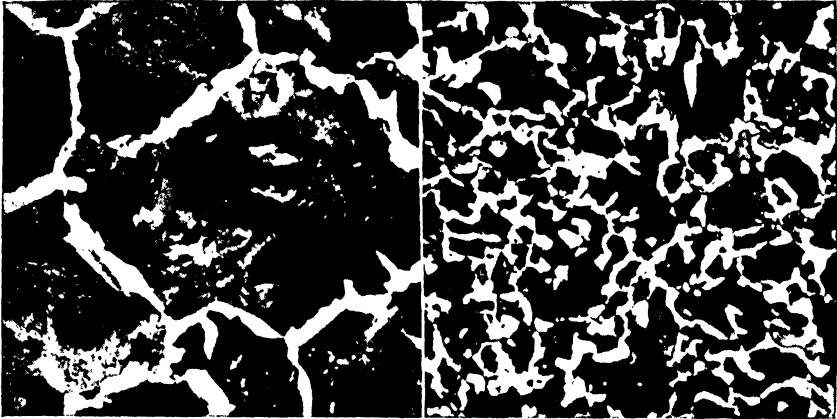

FIGURE 13.4. Grain refinement by annealing, 200×. Carbon 0.60%. Left, as cast; right, annealed.

above Ac_1, to which the metal is heated and the longer it is held at that temperature, the fewer and coarser the grains of austenite will become by their own interaction. Much theory and discussion has been written on this subject of grain growth, but for present purposes it is sufficient to accept the fact as stated. However, it will be seen that in order to get maximum effect of grain refinement by annealing, it will be necessary to keep the maximum temperature from going more than a few degrees above Ac_3 and to hold the piece at that temperature only long enough to be sure of heating it uniformly throughout. This should be about fifteen minutes for each inch of section thickness.

As a preparation for hardening, the effects of full annealing are not much different from those of normalizing. If the material is to be machined, prior to hardening, it should be annealed rather than normalized. Annealing is sometimes applied as the sole heat treatment of large steel castings where softness and refinement of grain are desired.

Where normalizing from a high temperature has been used as a homogenizing treatment, the grain may have been coarsened some-

what. In this case an anneal or another normalizing treatment may be given for the purpose of grain refinement.

Process annealing should not be confused with full annealing. It is used on wire and sheet steels during the drawing or rolling. These very small or thin sections are worked at temperatures much below the lower critical temperature (Ac_1), severe cold working strains are set up, and the metal becomes work-hardened. This condition is relieved at intervals by heating to some temperature just below Ac_1. The metal becomes not quite so soft as if it were fully annealed. The rate of cooling is not a factor in process annealing, but the material is usually cooled out of contact with air as much as possible to avoid severe surface oxidation.

Hardening by Quenching

If we heat a piece of carbon steel to some temperature above its upper critical temperature (Ac_3) and cool it very rapidly by plunging it into cold water, its hardness will be very noticeably increased. If the steel contains more than about 0.40% carbon, it will be glass hard and quite brittle. It can usually be cracked with a hammer and may even crack spontaneously as a result of the severe heat treatment.

There are a few uses for steel in just this fully hardened condition, such as for files and for the little wheels in glass cutters. Sometimes hardened steel pieces are used to resist abrasion or wear. In most cases, however, the hardening treatment is followed by tempering to give a more ductile, tougher product.

Because of severe treatment, the tendency to crack, and the necessity for uniformity of hardness in the finished piece, much care must be taken in the hardening operation and in the selection and preparation of the steel for hardening. *The best condition for a piece of steel, prior to hardening,* is that of having a uniform composition, with no segregation, or banding of impurities in streaks, through the metal. If it is hypoeutectoid steel, it should show a fine network structure of ferrite, surrounding small islands of pearlite, and these should be fairly uniform in size. It should, of course, be as free as possible from non-metallic inclusions, blowholes, surface defects, or pipe. It should be, as far as possible, of uniformly thick section, with no sharp notches or reentrant angles.

This last statement is a matter for the consideration of the designer, who quite frequently is unacquainted with the metallurgical features of his problem and assumes that heat treatment can always be properly accomplished by others. The heat treater, on the other hand, will try to meet well-nigh impossible requirements rather than admit his in-

ability to cope with them, and the result is much wasted time and material, and a product that is not as it should be. When designing intricate shapes (die blocks, unusual machine parts, and the like) that are to be heat treated, one should consult freely with the heat treater or metallurgist so that, without impairing the usefulness of the article, the heat treatment may be made as easy as possible and the best results may be obtained.

Causes of Cracking

Heat treating, particularly as regards the hardening operation, is as much an art as a science. The personal factor has never been entirely eliminated, and it is surprising how small variations in procedure make great differences in the quality of the finished product. There is the matter of rate of heating prior to quenching. It must be remembered that steel undergoes a big volume change in passing through the critical range. On cooling there is an expansion of 1.2% and on heating a similar contraction. Since all heating or cooling is from outside of the piece, that portion undergoes the transformation first. The result is that the outside of the piece is put in severe lateral tension upon heating through the critical range; and upon cooling, the outside is put under compression. The tendency to form cracks would, therefore, seem to be greater during the heating operation. And so it is, and notwithstanding the severity of the quench in water from the high temperature, the metal can usually stand it if the heating has been slow and careful. But the surest way to cause a piece to crack on quenching is to heat it too fast. The practice recommended is to allow one hour for each inch of section thickness in bringing the piece up to temperature, and to hold the piece at the maximum temperature for one-fifth of the total heating time to allow the temperature to become uniform.

Quenching Media

This subject is a large one for a short discussion. The important consideration regarding any quenching material is the rate of cooling. Without considering such an unusual substance as liquid air, the cooling velocities of various media are as follows:

1. 15% sodium chloride brine (fastest).
2. 5% NaOH solution.
3. 10% calcium chloride brine.
4. Water.
5. Mineral oil.
6. Cottonseed or olive oil.
7. Sperm or neatsfoot oil.

Water loses its quenching power rapidly as its temperature rises. The values given are for comparatively slow agitation or motion of

the piece in the quenching medium. Much more rapid quenching may be obtained, for instance, by having the piece struck by jets of water on all sides.

The selection of quenching media will depend on the hardness desired, the ability of the piece to withstand the shock of quenching, and economic considerations. The oils are expensive, particularly the animal and vegetable oils, and if the amount of work is large, a large supply of the quenching material must be kept because of the heat that must be dissipated.

The problem of cooling the oil is important, and somewhat elaborate methods have been devised. The practice of bubbling air through the oil is not desirable because the air bubbles get on the piece and cause little soft spots. The most approved method consists in piping the oil away from the quenching tank to a heat exchange reservoir where either cold water may be used to cool pipes through which the oil is circulated or the oil may flow around cold water pipes. In either method, after the oil is cooled, it is piped back to the quenching tanks.

Tempering or Drawing

The two terms are synonymous and refer to the process of reheating the previously hardened piece. The effect is simply to reduce the extreme hardness obtained by quenching. The amount this hardness should be reduced depends upon the use to which the material is to be put and is usually specified within close limits. Tempering temperatures are lower than the critical range, never reaching Ac_1, and the amount that the hardness is reduced depends on the temperature reached and the time the piece stays at the temperature. The rate of cooling has very little effect on the results.[3]

As the piece becomes less hard it also acquires greater ductility and toughness, the first noticeable effect being reached at about 250°C. After heating above 650°C, the piece is fully drawn and, regardless of its initial hardness, will be only moderately harder and tougher than in the full annealed condition.

Tempering .(or drawing) is in general a simpler operation than hardening. It may be controlled by pyrometric methods, by baths of molten materials maintained at the proper tempering temperature, or by the time-honored method of temper colors. The temper color method is the old time blacksmith's method and is convenient where pyrometers are not available.

[3] However, see remarks on temper brittleness, Chapter XXI, under Molybdenum Steels, page 246.

Temper Colors

When a piece of polished steel is heated, a film of oxide begins to form at about 250°C. At first this is so thin that it is transparent and produces an interference color, like a layer of oil on water. As the temperature rises, this film becomes thicker and the color changes. The color starts as a pale yellow, then brown, purple, blue, and then colorless, then purplish pink, and blue again. Finally, the oxide film becomes so thick that it is no longer transparent and the surface assumes the natural oxide color of gray black. The second blue represents something better than 400°C. These colors are a fair indication of the extent of tempering because they, like tempering, depend on the temperature and the time.

Mechanical Properties Resulting from Heat Treatment

It should be remembered that, prior to tempering, the piece is in a severely strained, hardened condition. For best results the heating should be slow; otherwise warpage may result. Warpage is another problem that the steel treater has to face. Uniformity and freedom from strains in the original steel do much to avoid it, but it cannot be dispensed with entirely. Where exact dimensions must be maintained, the surfaces are usually ground after heat treating.

What mechanical properties will actually result from a given heat treatment cannot be safely predicted, because they are affected by so many variables in addition to the chemical composition (as ordinarily determined) and the specific heat treatment employed. Thus, the grain size of the austenite prior to quenching, the type of quenching medium employed, the furnace atmosphere, the quality of the metal as regards undetermined impurities (H, O, N, etc.), and the steelmaking process and type of deoxidation used may all be expected to affect to a considerable extent the properties of the final product.

The charts shown in Figure 13.5 are redrawn from physical-property charts published by the International Nickel Company and the Bethlehem Steel Company. Because of the uncertainties listed in the previous paragraph the use of such charts as guides to specific heat-treatment operations is now discouraged. However, as illustrative of the range of properties obtainable in carbon steels by heat treatment, they seem to have educational value and so are included here.

The types of steels shown are used for forgings and structural parts of automotive apparatus. They are used wherever combinations of strength and toughness are desired, and in such parts as axles, frames, connecting rods, housings, and steering parts. The softer or lower-

carbon varieties will be used in static loading where structural adjust-
ments may be necessary and where no harm will result if a small
amount of bending or distortion occurs. Pieces that are occasionally
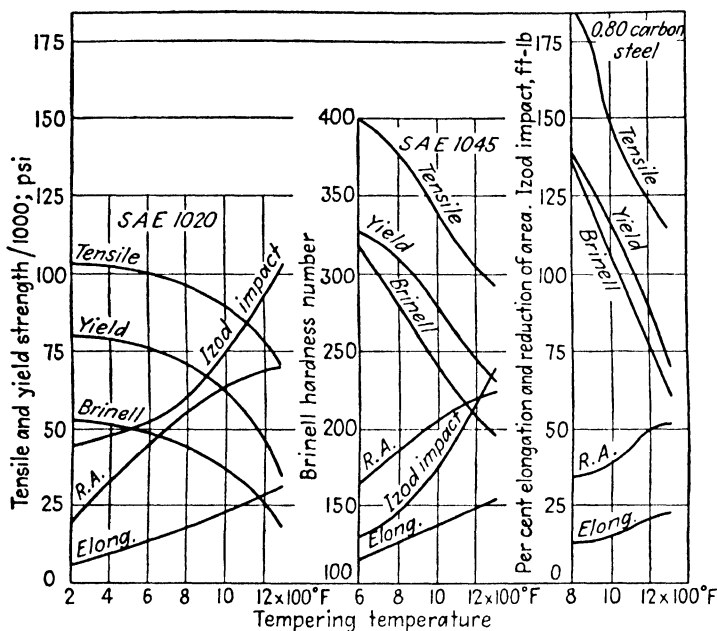subjected to an overload should bend before they break. Moving parts

FIGURE 13.5. Physical property charts for carbon steels, water quenched.
(Charts for SAE 1020 and SAE 1045 redrawn from "Nickel Alloy Steels," Sec-
tion 5, Data Sheet E, pages 14 and 15, 1946, The International Nickel Co., New
York. Chart for 0.80% carbon steel redrawn from "Bethlehem Alloy Steels," Booklet
211, 1946, page 31, Bethlehem Steel Co., Bethlehem, Pa.)

subject to dynamic stresses, on the other hand, should be made of the
harder materials. In all events, an adequate factor of safety should
be used.

It will be noted that often the same properties may be obtained in
different steels by suitable adjustment of the heat treatment. Here,
experience and judgment are the only true guides. It seems to be the
rule, however, that a steel with a little too high a carbon content,
tempered to a higher temperature, is more satisfactory than a steel
of too low a carbon content in a more severely hardened condition.

Constructional Steels

This term usually refers to any type of steel used in structures,
whether these structures are fixed, as in bridges or buildings, or dy-

namic, as in automotive machinery. Constructional steels ranging in carbon content from 0.30% to about 0.50% are frequently heat-treated. Steels containing less than 0.30% carbon are usually used in the rolled, forged, or normalized condition. A few composition limits for such steels are listed in the following table.

TABLE 1. Some Low-Carbon Steels

Uses	Composition limits, per cent			
	C	Mn	P	S
Wire............................	0.07 max	0.35-0.45	0.04 max	0.045 max
Rivets..........................	0.08 max	0.35-0.45	0.04 max	0.045 max
Sheet bar......................	0.07-0.10	0.35-0.45	0.04 max	0.045 max
Plate...........................	0.08-0.12	0.35-0.45	0.04 max	0.045 max
I beams, channels, etc........	0.15-0.20	0.35-0.50	0.04 max	0.045 max

Society of Automotive Engineers (SAE) specifications [4] are broader than these and cover all possible carbon contents up to 1.00%. A steel that finds wide application in the un-heat-treated condition is SAE 1020. The carbon range for this steel is 0.175% to 0.225%, with manganese from 0.30% to 0.60%. The fifth steel listed above comes partly within this specification. SAE 1020 steels are used for almost every conceivable purpose that requires a mild steel.

An important use for the SAE 1020 steels is in case carburizing. In this process steel articles are given a high-carbon surface by being heated for a period of several hours in a carbonaceous material such as charcoal. This is a very interesting branch of heat treatment that will be discussed in Chapter XVI.

Constructional steels containing more than 0.50% carbon are not frequently hardened and tempered but are used in the normalized, annealed, or rolled condition as for rails and railroad-car axles. Such steels are used in the making of heavy sections where heat treatment is difficult or costly, the strength and hardness being obtained as the result of composition alone.

Steels that range in carbon content from 0.60 to 1.40% are generally used in the heat-treated condition for tools and springs. Tools are frequently lightly tempered, and hardness is paramount. This is particularly true of woodworking tools, lathe tools, and fine cutting tools such as penknives, plane bits, and razors. Tools having heavier duty to perform, such as cold chisels, rock drills, chipping chisels, forging dies,

[4] See pages 224 and 225.

and large milling cutters will require less carbon and higher temperatures. Tools like hammers, sledges, bolt and rivet headers, and blacksmith's tools will be still softer. Naturally, tools that must come into contact with high temperature work cannot depend on severe heat treatment to maintain their hardness.

Definitions

1. *Hardening.* Heating a piece of steel to some temperature above the upper critical (Ac_3) and cooling it rapidly in water, brine, or oil for the purpose of increasing the hardness.

2. *Water Hardening, Oil Hardening, Brine Hardening.* Terms that refer to the medium used in the hardening quench (see Definition 1), brine hardening being considered the most severe and oil hardening the least severe treatment.

3. *Tempering or Drawing.* Reheating the hardened piece to some temperature below the lower critical temperature (Ac_1) to reduce the hardness a desired amount. Temperature and time are both factors in determining the extent to which the hardness is reduced.

4. *Temper Colors.* Interference colors that begin to form on a bright steel surface at a temperature of about 250°C. They likewise depend on temperature and time (see Definition 3) and can be used as a means of estimating the extent of drawing.

5. *Normalizing.* A conditioning operation consisting of heating the piece to about 100°F (55°C) above the upper critical temperature Ac_3 and allowing it to cool in air. This relieves rolling strains, refines grain, and reduces local segregation.

6. *Full Annealing.* Heating the piece to some temperature above (Ac_3) and cooling it very slowly in the furnace. This produces effects similar to normalizing but leaves the metal in a softer condition so that it can be more easily machined prior to hardening.

7. *Process Annealing.* Reheating work-hardened sheets or wire to near the lower critical temperature to soften them.

8. *Homogenization.* The reduction of segregation by allowing diffusion to proceed above Ac_3, a higher temperature being employed than in normalizing (see Definition 5).

QUESTIONS ON THE TEXT

1. What is meant by recalescence? by thermal hysteresis?

2. Explain in words the meaning of each of the following symbols: Ac_3; Ar_1; Ar_{cm}; Ar_2; Ac_1.

3. How does normalizing differ from homogenizing; from full annealing?

4. Explain grain refinement by annealing. What *grain* is refined?

5. To what is the tendency to crack upon quenching due?

6. Explain temper colors.

SUPPLEMENTARY QUESTIONS AND PROBLEMS

1. Why will recalescence not take place in low-carbon steel?

2. Case carburizing operations (Chapter XVI) indicate that carbon will diffuse through austenite at heat-treating temperatures at the rate of about 0.10 inch in 8 hours. At this rate how much time is required to change pearlite to austenite if the lamellae of cementite are 0.5 micron apart?

3. From the volume expansion in the change from gamma to alpha iron (given in the text) calculate the change in interatomic distance. In which allotropic form is this distance the greater?

4. Describe the complete heat treatment of a screw driver containing 0.60% carbon. To what temperature would you temper it?

EXPERIMENTS

1. Heat a piece of steel clock spring or music wire in a hot gas flame until the piece glows bright red and then watch it cool in a dark place. Note and explain the phenomenon of recalescence.

2. Quench a piece of spring from just above the recalescence temperature and another from just below that temperature and try to bend each piece.

3. Stretch a piece of music wire (about 22 gage) between nonconducting supports, say 5 feet apart. Pass a current through the wire to heat it bright red and watch it sag. Shut off the current and observe the contraction. Explain its behavior.

The Microstructures of Heat-Treated Steels—Theories of Hardening

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Diffusion of Carbon during the Transformation · The Effect of Rapid Cooling · The Effects of Cooling Rate · The Split Transformation · Subcritical Transformation: the S Curve · S-Curve Structures · Hot-Quenching Methods · The Hardness of Steel

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So far we have considered the microstructures of steels that were cooled quite slowly through the critical range. These structures were characterized by islands of pearlite surrounded by white networks of ferrite, in the case of hypoeutectoid steels, or of cementite in the case of hypereutectoid steels. The mechanism of the formation of these structures was described for hypoeutectoid steels as consisting of the crystallization of the ferrite at the grain boundaries of the austenite when the latter was cooled through the transformation range. The composition and temperature of the austenite was described by the Ar_3 line. In the case of hypereutectoid steels a similar precipitation of *cementite* took place, the composition and temperature of the austenite being described by the A_{cm} line. The intersection of the Ar_3 line and the A_{cm} line is the eutectoid point, and austenite of this composition and temperature changed, on cooling, to the finely laminated pearlite.

Diffusion of Carbon during the Transformation

This all took place in an orderly fashion. Now when we consider that the solid solution, austenite, was decomposed by this process into

two new phases, and that one of these phases contained all, or practically all, of the carbon, which we can assume to have been distributed quite uniformly in the austenite, it is clear that an actual migration of the carbon took place during the transformation. This migration is a matter of diffusion which in the solid state is necessarily slow.

In the preceding chapter we considered the physical effect of cooling steel through this transformation range with great rapidity. What may we expect to happen to the microstructure when this occurs? Will it be similar to the slowly cooled structure but finer? This is not probable, for the coarseness of the meshes in the network is determined by the size of the austenite grain, and that is formed before the quenching takes place. The effect of rapid cooling will appear in those changes that require time. Such changes are those due to carbon diffusion. The formation of the carbide (cementite) in the pearlite requires diffusion of carbon in the austenite, so we should expect the formation and distribution of this carbide to be greatly affected by the quenching.

FIGURE 14.1.   The structure of quenched steel—martensite, 500×.

The Effect of Rapid Cooling

If we examine a steel of any carbon content, that has been quenched from above Ac_3, it will show a structure that is in no respect similar to the annealed steel. A hardened steel becomes etched more slowly than the same steel slowly cooled, but if we etch it long enough to

develop a structure we will see at moderate magnification (200 to 600×) what appears somewhat like a pile of straw, straight or needle-like features, all mixed up (Figure 14.1). If the temperature, prior to quenching, was quite high, the straw pile structure may have a sort of regularity. The straws, or needles, are frequently arranged in parallel groupings that suggest an alignment with crystallographic directions similar to the Widmanstätten structures of cast steels. For the most part, however, the structure is mussy and ill-defined. It is frequently referred to as an "acicular" (meaning needle-like) structure.

The Acicular Structure

High magnifications sometimes give a more definite appearance to the structure. When the needles are distinct, close examination of each needle indicates that it consists of a dark central line surrounded by a lighter gray area of elongated oval shape (Figure 14.2). The background or matrix for these features is white and featureless except for a slightly wrinkled appearance, but the amount of the needle-like features varies from a few fairly well isolated needles to a mass in which no background at all is visible. This variation is associated with the speed of the quenching; the more rapid the quenching the fewer the needles found in the structure.

The interpretation of these features is still a matter for considerable discussion among physical metallurgists, and no attempt will be made here to explain them. Let it not be supposed that they represent any great or sharp variations in the physical character of the material or in composition as, for instance, exists between the cementite and ferrite of pearlite. As a matter of fact, the attack of the etching reagent is very light, even at the black centers of the needles. Scratches on the surface show no noticeable variations in hardness at the centers of the needles and in the matrix.

FIGURE 14.2. Martensite needles at high magnification, 2000×.

Martensite

Hardened steel that exhibits this straw-like, needle-like structure is called martensite. It is the hardest form of steel. It is not obtainable in low-carbon steels, or at least, it is not stable at ordinary temperatures if the carbon is low. Martensite is a highly metastable form although not, strictly speaking, an allotropic form or phase.

The x ray indicates three types of space lattice in martensite. There is usually present a small amount of untransformed austenite which is indicated by the face-centered cubic lattice. This may be eliminated by cooling in liquid air or by aging. The predominant lattice is body-centered cubic which is the same as that of alpha iron, or ferrite. A small amount of body-centered tetragonal[1] lattice is found in freshly formed martensite. This may be eliminated by heating to the temperature of boiling water. It is probably body-centered cubic material under high stress.

Martensite seems quite stable and unchangeable at ordinary temperatures except for the fact that it increases slightly in hardness by aging for about two weeks, or by heating in boiling water for about five hours. This may be due to the completion of the transformation of the austenite. Not until it is heated to about 250°C does it show any noticeable decrease in hardness or change in structure.

Tempered Structures: Troostite

However, at about the temperature where the temper colors begin to show on the brightened surface of a piece of martensitic steel, it begins to change its properties and microstructure; the former gradually with temperature, but the latter, abruptly. The entire specimen begins to take on a yellowish or brownish tint with ordinary etching. As the tempering temperature is increased to about 400°C, the etching time becomes much shorter and unless care is exercised the specimen becomes so black as to appear featureless. However, with light etching, the acicular structure persists in specimens tempered as high as 550°C. Great care must be taken with such specimens to avoid abrasion of the surface which has a sooty layer that may be damaged even by a stroke from a soft camel's-hair brush.

This structure, when first observed, was called troostite and the name persists in spite of attempts to revise the rather unsatisfactory

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[1] The tetragonal lattice has three axes at right angles to each other. Two of these axes are equal. The third is longer or shorter than the other two. It thus results in square-section prisms instead of cubes. Brief consideration should reveal that whether the lattice is body-centered or face-centered depends only on how the axes are chosen.

nomenclature of steel structures.[2] It is properly applied to the dark etching structures first appearing upon the tempering of martensite.

Troostite probably represents the first actual precipitation of iron

FIGURE 14.3. Steel hardened and tempered to 400°C—troostite, 500×.

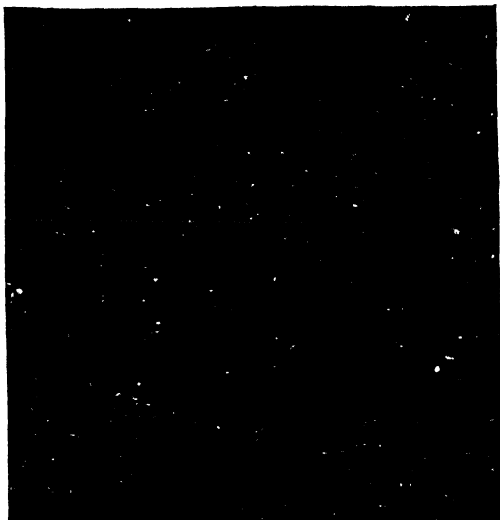carbide (cementite) from the erstwhile ferritic solid solution. In martensite the space lattice has changed on the original quench to that of body-centered ferrite, but there has been no chance for the migration of the carbon necessary to form discrete particles of cementite. Upon heating, this latter occurs, producing at first a colloidal or submicroscopically fine precipitation of the carbide particles. The etching characteristic of troostite is probably due partly to relieving these particles at the surface, and partly to staining by oxidation, because of the very rapid attack by the acid on this very fine, two-phase structure.

As might be expected, the physical properties of troostite vary with the temperature to which it is heated. Starting with slightly less hardness than the martensite from which it formed, it becomes softer as the temperature rises. As soon as it is soft enough to show a tensile strength without cracking and an elongation and reduction of area, these also are found to vary with increasing tempering temperature, tensile strength and yield point decreasing, and elongation and reduction of area increasing.

Sorbite

With still further increase in tempering temperature (550° to 600°C), the etching begins to take on a cleaner, better defined appearance. It is no longer easily erased by a rub with the finger. The acicular pattern has become so diffuse that it is practically undetectable. At magnification of 500× or better, the structure is a little like that of a pearlitic steel at magnifications of less than 100× but lacks the

[2] "On Naming the Aggregate Constituents in Steel," by J. R. Vilella, G. E. Guellich, and E. C. Bain, *Trans. Am. Soc. Metals,* 24, June, 1936.

appearance of the pile of leaves, attributed to the pearlite. High magnification does not resolve any ferrite or cementite, and with hypoeutectoid or hypereutectoid steel there is no network or boundary material.

This structure is called sorbite. It is softer, more ductile, and of lower tensile strength than troostite, but still tougher and harder than the annealed pearlite structures.

Modern microscopic methods have encroached more and more upon the so-called unresolvable structures, so that it has been thought
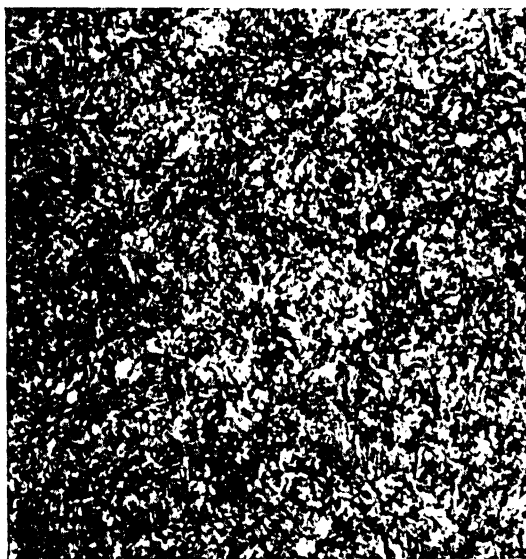
FIGURE 14.4. Steel hardened to 600°C—sorbite, 500×.

advisable to revise the nomenclature of these structures so as to omit resolvability as a criterion. It was proposed by E. C. Bain that all structures produced by the reheating of martensite be called sorbite, the term troostite being reserved for quenched structures that are intermediate between pearlite and martensite. However, the term troostite has persisted as applied to the dark etching structures that result from the reheating of martensite to a low temperature.

Spheroidite

Finally, if we hold the temperature of the specimen for a protracted period of time just below A_1 (723°C) but do not exceed that temperature, the structure will still be sorbite but higher magnification will show discrete particles of cementite embedded in a matrix of ferrite.

The particles will be rounded, not plates as in the case of laminated pearlite.

This structure, usually classed as sorbite, is sometimes misnamed granular pearlite. Spheroidite is a better name. Cementite in the form of rounded globules is called spheroidized, or *divorced,* cementite.

It must be evident that there are several points of difference between such a structure and pearlite, although the physical properties approach those of a pearlitic steel. The spheroids of cementite are scattered uniformly through the matrix, regardless of carbon content. Hence there is no definite pearlite composition. Spheroidite cannot show the iridescence attributed to pearlite because it is not finely laminated. In some respects it is superior to annealed steel of the same over-all physical properties because of the uniformity of the structure.

We have, therefore, four heat-treated steel structures, known as the transformation stages. These are shown in Table 1.

TABLE 1

Structure	Hardened and drawn to	Appearance	Physical properties
Martensite......	below 250°C	Needles or straw	Very hard, brittle
Troostite........	250°–550°	Dark to mottled	Hard, not so brittle
Sorbite.........	550°–650°	Leafy texture	Tough and ductile
Spheroidite (granular pearlite)......	700°–725°	Spheroidized cementite	Almost as soft as if annealed

Some of the early investigators in metallography had a rather naive theory that steel acquired a sequence of structures when quenched and that it had to pass through this same sequence in reverse order when it was reheated. This led to double applications of the terms pearlite, sorbite, and troostite. As applied to cooling, the rate determined the structure. Thus slow cooling produced pearlite; more rapid cooling, sorbite; still more rapid, troostite; a severe water quench produced martensite; and it was believed that, if the cooling could be still more rapid, room temperature austenite would result.

It is now known that this theory was erroneous, and that the mechanisms of transformation on cooling are different from the mechanism of the tempering of martensite. Furthermore, the cooling structures do not even resemble very closely the reheating structures, and it is rather surprising that the early investigators were so easily influenced by these preconceived ideas and undigested theories. However, in their

defense, let it be noted that the identification and differentiation of microstructures is exceedingly difficult in the absence of a sound theory regarding the cause of the structures. No two patterns look exactly alike under the microscope, and names were given to structures that later investigation showed to have no basis of distinction. In addition
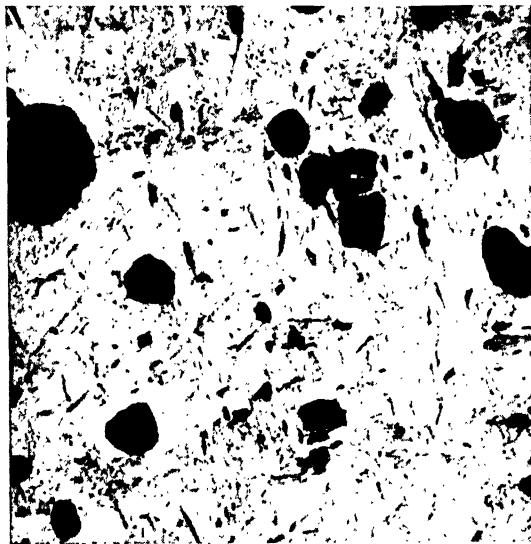

FIGURE 14.5.   Nodular fine pearlite and martensite, 500×.

to sorbite, troostite, and martensite, there were hardenite and osmondite; when the observer found it difficult to classify his patterns he compounded such terms as "martenso-troostitic," "troosto-sorbitic," and even "sorbito-troostitic," the distinction being of a high order of refinement.

The Effects of Cooling Rate

Present day terminology lists three distinct structures that can be obtained in steel by appropriate cooling rates. The first, obtainable by slow or moderate cooling, is pearlite. This is the structure described in Chapter IX, where the eutectoid ferrite and cementite alternate in sheets and appear as parallel wavy lines in the microsection. The higher the rate of cooling the finer and more wavy the lines become. In extreme cases they cannot be resolved by the ordinary microscope, but the mottled, leafy structure, characteristic of more slowly cooled pearlite at lower magnifications, is discernible in the finer pearlite at high magnification, and the electron microscope

has definitely demonstrated that this structure is still lamellar pearlite. Under these conditions it is qualified as *fine pearlite.*

Complex Structures: Nodular Fine Pearlite

In carbon steels fine pearlite and martensite can occur together. When this happens the patches of fine pearlite frequently appear as rosettes surrounded by the martensite. If the etching has been sufficiently long to show the acicular structure of the martensite, the
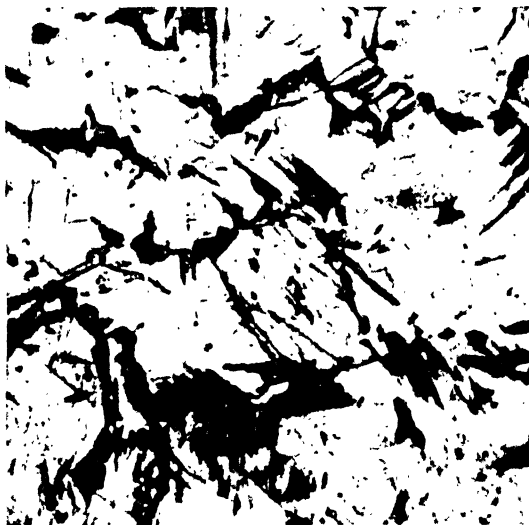

FIGURE 14.6. Bainite (dark) and martensite (light) in quenched steel, 500×.

rosettes will have become hopelessly over-etched and appear as black nodules. This is the explanation of why, in older terminology, they were called "nodular troostite." At present the accepted term for this structural feature is nodular fine pearlite. (Figure 14.5.)

Martensite and Bainite

When the cooling rate becomes so great that pearlite does not have time to form, the normal structure in carbon steels is martensite. However, in many alloy steels and with certain critical cooling rates in carbon steels, a series of structures that are neither pearlite nor martensite is obtained. Yet they do not resemble the troostite or sorbite of reheated martensitic steels. These new structures are acicular or lath-like, dark etching, and, when produced by ordinary quenching, are usually associated with martensite and sometimes with pearlite. Explanation and analysis of these structures in terms of the transformation of

austenite and precipitation of the carbide phase will be presented after the discussion of the S curve.[3] In spite of Dr. Bain's suggestion[4] that the term troostite be reserved for these structures, custom and usage have firmly attached to them the term *bainite*. (Figure 14.6.)

The character of martensite has been discussed. Since it decomposes on heating to form troostite, it is a unique structure, for no other structure produced by some other treatment is at all like it.

The Split Transformation

The cooling structures may be tabulated as in Table 2.

TABLE 2

Rate of cooling	Suggested medium	Name of structure	Physical characteristics
Very slow	Furnace	Pearlite	Soft and ductile
Gentle	Air	Fine pearlite	Tough and ductile
Rapid	Oil	Fine pearlite, bainite, and martensite	Hard and somewhat ductile
Fast	Water	Bainite and martensite	Hard
Very fast	Water jets	Martensite	Very hard

In 1919 Portevin and Garvin[5] published the results of studies in which time-temperature cooling characteristics of steels were determined at various speeds of cooling. The results were very enlightening at that time. As the rate of cooling is increased the critical temperatures are lowered progressively below the temperatures at which they occur in slowly cooled steels. This is in keeping with the lag or thermal hysteresis discussed before. With such undercooling it becomes increasingly difficult to identify the different steps in the transformation, that is Ar_3, Ar_2, Ar_1; but the critical point is characterized as a place of minimum slope in the curve (Figure 14.7).

Now it is found that when the rate of cooling becomes so great that the critical point is lowered to about 650°C, another delay appears at about 300°C. As the rate of cooling is still further increased the upper change continues to become lower but becomes less and less intensive while the lower one increases in energy. By the time the upper effect has been reduced to about 550°C, it disappears altogether.

[3] "The Transformation of Austenite at Constant Subcritical Temperatures," by E. S. Davenport and E. C. Bain, *Trans. Am. Inst. Mining Met. Engrs.*, Tech. Pub. n. 348 (1930).

[4] See footnote 2, page 138.

[5] "The Influence of the Rate of Cooling on the Hardening of Carbon Steels," by A. M. Portevin and M. Garvin, *J. Iron Steel Inst.*, 99, 469 (1919).

Examination of the structures obtained with these different rates of cooling will show pearlite or fine pearlite where the transformation occurred at the higher temperature, and bainite or martensite where it occurred at 300°C or less. The relation of structure, rate of cooling, and transformation temperatures are shown in Figure 14.8.
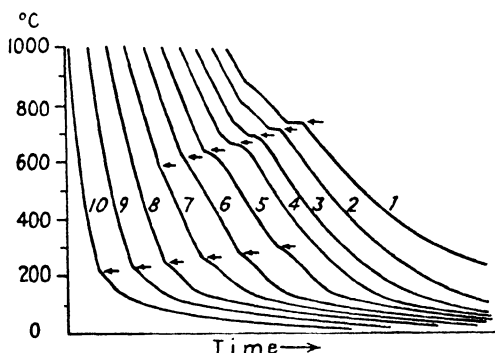
FIGURE 14.7. Curves 1, 2, 3, etc., represent progressive increases in the rate of cooling.
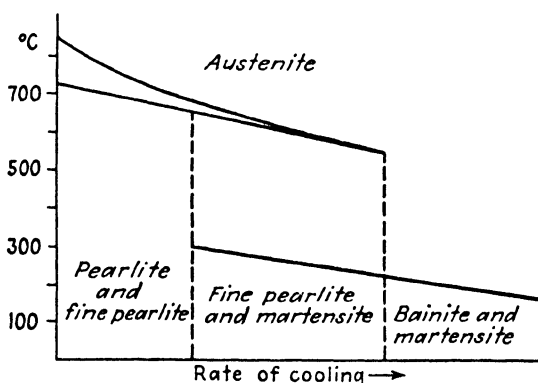
FIGURE 14.8. Effect of cooling rate in splitting the transformation into two states.

This phenomenon is known as the split transformation. It offers a simple explanation of those structural changes in steel that are due to sudden cooling. This is as follows:

When the steel is cooled rapidly from above the transformation range, the tendency for the austenite to transform to alpha iron and for cementite to precipitate is blocked by a tendency toward undercooling. If the undercooling does not extend below 550°C it results in a laminated pearlitic structure, the fineness of which depends on the

temperature at which the transformation occurs. When, on the other hand, the rate of cooling is still more rapid, the austenite is cooled to below 550°C without change. Due possibly to increased rigidity, the tendency to change is not as great below 550°C as above, and practically no change takes place until a much lower temperature is reached. Then the crystal structure changes spontaneously, leaving the carbon scattered through the metal in a supersaturated solid solution of carbon in alpha iron. This is the best conception we have of the nature of martensite. Reheating the quenched specimen slowly to 250°C or 300°C results in a sort of colloidal precipitation of the cementite which gives rise to the structure of troostite. If the cooling rate is just right the change of space lattice and precipitation of the cementite may both take place, before the specimen is quite cold, on the original quench. This explains the lower line of the split transformation.

It will be seen that the form of the precipitated iron carbide is different when it is produced by reheating the martensite from that which occurs as laminations in pearlite. The laminated structure depends on the ferrite and cementite being formed simultaneously by the decomposition of the solid solution, austenite. In martensite, however, the ferrite is formed first, and the cementite is precipitated from solution in the ferrite. Cementite, precipitated in this manner, forms the small rounded particles which characterize the troostite, sorbite, and spheroidite of the tempered steels.

Subcritical Transformation: the S Curve

In an epoch-making article [6] published in 1930, E. S. Davenport and E. C. Bain described their researches on the transformation of austenite at constant subcritical temperatures. Their ingenious method threw much light on the behavior of steels during quenching and the structures produced and gave values that could be translated quantitatively into cooling rates and tempering temperatures.

Their procedure was indeed simple and as follows. Small pieces of the steel to be studied were heated in a furnace to some temperature sufficiently higher than Ac_3 to insure their becoming uniformly austenitic. Each piece was then quenched, first in a bath of molten lead or low-melting alloy, held at some constant temperature below Ar_1, then in cold water or brine. The time in the metal bath was increased for successive specimens on a logarithmic scale varying from a few seconds to hours, days, or weeks. Microsections were then made of the pieces and quantitative measurements of the proportions of certain

[6] See footnote 3, page 143.

structural features were plotted to form a very interesting and instructive curve, Figure 14.9.

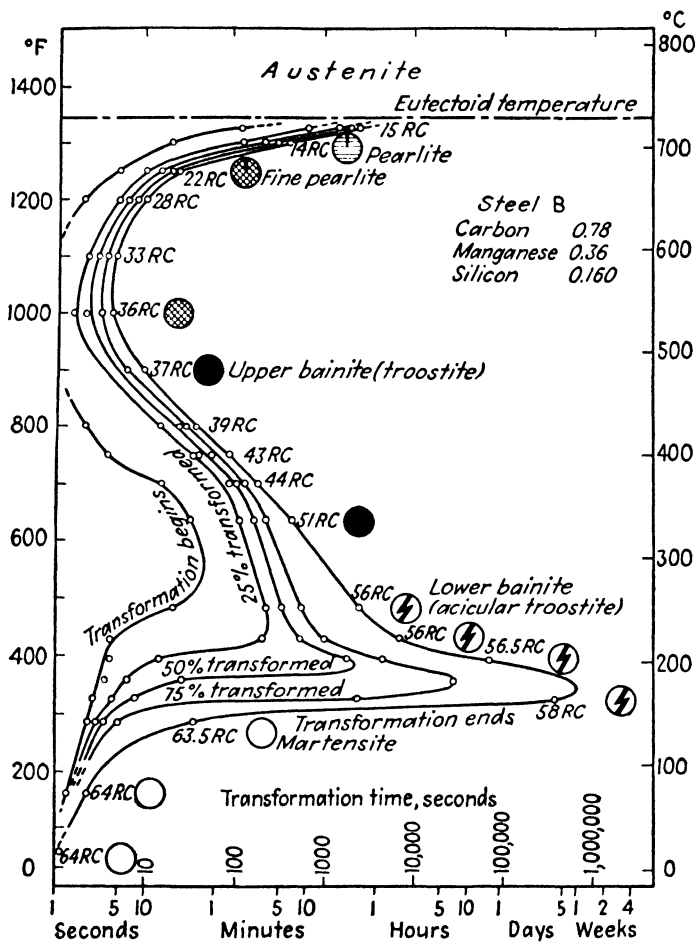To understand the curve, we may consider what happens to the

FIGURE 14.9. S curve for eutectoid steel. Rockwell C (RC) hardness values are for the steel completely transformed at indicated temperature. Symbols ○ at right of curves indicate product of transformation. (From "Transformation of Austenite at Constant Subcritical Temperatures," by E. S. Davenport and E. C. Bain, *Trans. Am. Inst. Mining Met. Engrs.*, 1930.)

structure of a piece of eutectoid steel when subjected to the two step quenching treatment just described. First, let it be noted that the molten metal bath gives a very rapid quench even though the final temperature is not low. This cooling rate exceeds the rate of transformation of the steel so that it remains austenitic until the cooling

halts [7] at the temperature of the metal bath. After the allotted time interval, the transformation proceeds and may be partially or fully completed.

The second quench in water or brine transforms any remaining austenite into martensite. The products of transformation at the temperature of the metal bath are easily distinguishable microscopically from the martensite.

We can thus make a record of the progress of transformation at any temperature at which we choose to hold the metal quenching bath between 300°C and the critical temperature. Davenport and Bain plotted such information on a graph, making time the abscissas and temperature the ordinates. Time was that during which the specimens remained in the metal bath and, consequently, also that required for the transformation to start, proceed, and complete itself at whatever temperature the bath was held.

The above method was not applicable at temperatures below 300°C because at these low temperatures the product of transformation was martensite and, hence, not distinguishable from the product of the water quench. The curve was continued, however, down into the low temperature range (even to room temperature) by plotting time-temperature expansion curves made with a dilatometer. Steel expands as it transforms on cooling and, by developing great experimental skill, the investigators made measurements of the rate at which martensite forms. Later studies have shown that the interpretation of their results in regard to martensite formation was somewhat in error and that, while martensite starts to form almost instantaneously, the amount formed depends on temperature rather than time.

The shapes of the curves are somewhat similar for all carbon steels and roughly resemble the letter S from which the name S curve is derived. Figure 14.9 shows a set of these curves for a particular steel.

Several curves are drawn, the one on the left representing the start of transformation, the one on the right, its completion. Points on the curves represent the time required for the transformation to start (or progress to the extent indicated) in austenite that has been cooled rapidly from above Ac_3 to the temperature level chosen.

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[7] Water quenching is very rapid because of the high specific heat of water, whereby a small amount of water in contact with the specimen can absorb much of its heat. In the metal bath, on the other hand, while the weight specific heat is not so great, perhaps only one-fourth that of the water, two factors make the heat-absorbing power greater than that of water. First, the volume concentration of heat-absorbing power is greater than that of the water because of the much greater density of the metal bath. Second, the transfer of heat from specimen to bath is greater because of the higher heat conductivity of the metal.

This curve is a compilation of data obtained in a specific manner, as above described. It is *not* a time-temperature cooling curve and it is *not reversible;* that is, it gives no indication of what happens on heating. Neither is it an equilibrium diagram. In interpreting such a curve one must be careful not to attribute such characteristics to it.

Such a diagram is, however, heavily laden with information. Methods have been worked out by which time-temperature cooling curves, drawn on the same chart, can be correlated with, and predicted by the S curve. More important, however, has been the information gained by the study of the microstructures produced by the transformation taking place at the various temperatures. Modern high-magnification methods have resulted in a much clearer understanding of what happens to rapidly cooled steel and have made desirable a revision of the classical nomenclature of steel structures.

S-Curve Structures

It is found that as the temperature of the transformation (the temperature of the metal bath) is progressively lowered below 723°C the structure of the pearlite, which was fairly coarse and straight lined when formed at high temperatures, becomes finer and more irregular or curly. The laminated structure continues to form, however, at temperatures as low as 500°C so that what was formerly called sorbite and nodular troostite (round radially marked areas appearing as dark patches in martensite) is in reality merely fine pearlite. (Figure 14.5.)

At temperatures between 500°C, which is a temperature of very rapid transformation, and the temperature at which martensite forms, the product of transformation is acicular but not martensitic. This is a new structure that cannot be produced by continuous cooling except in combination with martensite or pearlite. Isothermal transformation converts the entire specimen to this structure. Honoring its discoverer, it is now called *bainite.*

Reheating the fine pearlite for a short time does not change it appreciably, but reheating the martensite or bainite results in a coarser dispersion of particles, producing the sorbite or spheroidite of tempered steels. For this reason the terms troostite and sorbite are now applied only to reheated structures.

Hot-Quenching Methods

The high-temperature quenching in molten metal or salt baths, that was used in S-curve studies, has been adapted to several new heat-treating processes. These are generally referred to as *hot-quenching*

methods. Also, the time-honored process of *patenting,* which was used in the treatment of wire, has been improved upon by hot quenching.

Old-process patenting consisted in cooling the wire from above Ac_3 in hot air or other heated gases to about 650°C, holding at that temperature to allow the transformation to take place, and then air-cooling to room temperature. It is applied to wire containing not less than 0.25% carbon. The structure produced, formerly classed as sorbite, is that of fine pearlite. Quenching and holding in a lead bath at 650°C is said to give better results than the hot-air quench. Patenting produces tougher wires with less danger of cracking than the quench-and-draw method of heat treatment.

Another treatment, that was devised as the direct result of S-curve studies, is known as *austempering.* In this, the steel is quenched from the austenitic condition into a lead bath that is held at *any* desired temperature below the critical temperature and above that at which martensite forms. Time is allowed for the transformation to complete itself, after which the steel may be cooled in air. Any of the subcritical transformation structures with their attendant properties may be obtained in this way.

In case the time in the hot-quenching bath is less than that necessary for complete transformation, water quenching will change the residual austenite to martensite. This may then be tempered, resulting in a combination of structures. Such a treatment is referred to as *interrupted quenching.*

A modification of austempering, known as *martempering,* has been found very effective in preventing the cracking of tool steels on quenching. In this treatment the heated article is quenched to a temperature just above that at which martensite starts to form, and where the rate of transformation to bainite is very low. Holding at this temperature allows the temperature throughout the piece to become uniform before any transformation occurs. Then a comparatively low cooling rate from this temperature allows the entire piece to change to martensite, yet avoids damaging stress gradients.

These treatments are applicable only to small sections of carbon steels, usually not over ½ inch in diameter, or to alloy steels in which the rate of transformation is greatly reduced.

The Hardness of Steel

Jeffries' Slip-Interference Theory

The question, "Why is steel hard?" has bothered metallurgists since steel was first invented, but not until the question, "Why is steel soft?"

propounded by Dr. Zay Jeffries,[8] was the way pointed to a rational answer to both questions. Requiring 1537°C to break down its cohesive forces sufficiently to melt it and 3000°C to boil it at air pressure, it would seem that iron should have a hardness comparable to porcelain or glass, which it does only when hardened. Hardness and tensile strength are quite closely related and, if the melting temperature and boiling temperature of iron are an indication of cohesive force, which they are, pure iron should have a tensile strength much higher than any value obtained thus far for the strongest steel.

The reason advanced by Dr. Jeffries why we do not obtain the tensile strength, in pounds per square inch of section, that would be indicative of the cohesive force of the atoms across that section, is that in no test yet devised has it been possible to load the specimen in such a manner that the atomic forces were all brought to a maximum value at the same time. Rather do we break the bonds, a few at a time, by cracking in the case of brittle materials like martensite, a process analogous to the tearing of a piece of paper, or we allow the piece to reduce its section by flowing, as in the case of soft or annealed specimens. The manner in which this flowing occurs is interesting and offers a partial explanation of the way steels and other metals are hardened.

This flowing can only take place in a crystalline arrangement of atoms as a slipping of planes of atoms past each other. Metals made of atoms that are all alike can slip easily because, whatever the nature of the cohesive forces between them, these forces are not actually broken as in cleavage but merely transferred from atom to atom as slipping proceeds. The evidence of this slip is seen microscopically in slip bands, which are produced on a polished surface when the metal is subjected to mechanical strain beyond the elastic limit. These slip bands are sets of parallel bands, or lines that appear in each strained crystal grain and represent the offset, or faulting of the crystal along its slip planes. They disappear if the specimen is repolished and re-etched, showing that the sliding plane did not constitute a discontinuity or break in the atomic arrangement.

Slip goes on with comparative ease in a pure metal, even when the atoms are held together by tremendous forces, because the only places where these forces have to be broken is at the boundaries of the grains. These regions are few and small compared with the volume of the piece as a whole.

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[8] "Slip Interference Theory and the Hardening of Metals," by Zay Jeffries and R. S. Archer, *Chem. and Met. Eng.*, 24, 1057, June 15, 1921. Also see *The Science of Metals*, by Jeffries and Archer, McGraw-Hill Book Co.

Jeffries postulates, however, that anything that will interfere with this slip will act in a way to harden and increase the strength of the metal. He suggests two interfering devices; one, merely increasing the number of grains so as to have more grain boundary situations to

FIGURE 14.10.   Slip lines in ferrite (body-center cubic), 400×. (See also Figure 3.1.)

deal with; the other, to introduce some foreign particles to act as "keys" to prevent the planes of atoms from slipping.

These devices will actually work although not, perhaps, quite as effectively as Dr. Jeffries first thought. The hardening effect of cold work is the best example of the first method. Here the grains are crushed and battered up so that eventually, as in wire drawing, they become very small and numerous. It is often observed how all metals are increased in hardness by this method.

The second device is called precipitation, or dispersion, hardening. It offers a reason for the increase in hardness of a metal in which a second phase can be produced in finely divided form; by cooling a solid solution, for instance, so that its temperature, as represented on the equilibrium diagram, crosses a solvus curve and enters a heterogeneous region. The hardening of brasses, bronzes, aluminum alloys, and many others can be satisfactorily explained by this principle. In bainite, troostite, sorbite, and even pearlite, the toughening and hardening effects are due largely to the finely divided cementite. Naturally, the more finely divided the cementite the more effectively will

it key all sliding planes and thus harden the metal. Hence, troostite is harder than sorbite; sorbite is harder than spheroidite; and fine pearlite is harder than ordinary pearlite.

Space-Lattice Distortion

A third device, apparently overlooked by Dr. Jeffries, but very brilliantly suggested by K. Heindlehofer and E. C. Bain, in an article published in 1930,[9] is most simply described as a warping, twisting, or corrugating of the sliding planes themselves by keeping the metal in a strained condition. Certainly, layers of atoms that are very uneven and irregular cannot slip without rupture at a great many points, which rupture, of course, requires maximum stress. Such a condition must exist in martensite where each grain of ferrite, in addition to being under maximum compression or tension by surrounding grains, is unwillingly holding in highly supersaturated solid solution atoms of carbon, each of which must have a powerful distorting effect on the space lattice around it. Slip, under such conditions, is impossible and under severe external stress the piece cracks or breaks as a brittle material.

The most useful hardening effects are obtained when the warping, straining, and keying are reduced to a point where a small amount of slipping can adjust and smooth out uneven and locally concentrated stresses from external loads so that a maximum number of atomic forces are brought into play at one time to resist these loads. This condition is obtained in the troostite and sorbite of heat-treated steels.

QUESTIONS ON THE TEXT

1. Describe the structure of the martensite shown in Figure 13.6.
2. What is the only real difference between the troostite and sorbite of tempered steels?
3. Why is "granular pearlite" a rather poorly chosen name?
4. What is nodular fine pearlite?
5. How does bainite differ from fine pearlite; from martensite?
6. How is the split transformation explained by the S curve?
7. Explain work hardening; precipitation hardening; the hardness of martensite.

SUPPLEMENTARY QUESTIONS

1. Show by a sketch that a tetragonal lattice may be considered either face centered or body centered, depending upon how the crystal axes are chosen.

[9] "A Study of the Grain Structure of Martensite," by K. Heindlehofer and E. C. Bain, *Trans. Am. Soc. Steel Treating,* 18, (1930).

2. Why cannot a face- or body-centered cubic lattice be considered tetragonal by this scheme?

3. The growth of cementite particles in tempered martensite must be due either (1) to coalescence of small particles, that is, gathering together to form larger ones, or (2) to growth of the larger and more favored particles by solution of the smaller ones followed by diffusion of the carbon and reprecipitation onto the larger ones. Which mechanism seems the more likely? Why?

4. Describe a heat treatment that should result in proeutectoid ferrite plus martensite in a 0.50%C steel.

5. Using the S-curve diagram, explain why a carbon steel cannot be changed entirely to bainite by continuous cooling.

6. Why does heating to just below Ac_1 soften a steel that has been hardened by cold work?

The Physical and Mechanical Characteristics of Metals

Tensile Strength · The Tensile Test · Uses and Limitations of the Tensile Values · Young's Modulus · Poisson's Ratio · Hardness and Hardness Testing · Impact Testing · Fatigue and Fatigue Testing

Metals are useful substances for a great variety of reasons. The metallic properties (luster, opacity, malleability, ductility, and thermal and electrical characteristics) are utilized extensively, but properties also are utilized which are not uniquely metallic, such as hardness and strength. Engineering procedure seeks to classify metals and alloys as to these properties by measuring the properties and placing a numerical value upon them. This numerical value is taken as an indication of how the metals will behave in the service to which they are to be assigned.

Although this may seem simple enough in the matter of such things as tensile strength and ductility, it is somewhat difficult to devise a test that will show accurately the way the metal may be expected to behave in service. The test is rarely the exact duplicate of service conditions and, in matters of design, allowance must always be made for possible differences between the two.

Tensile Strength

From the standpoint of the design of structures and machines the most important properties to be dealt with in metals are those that have to do with the strength of the metal. The engineer of the past has assumed, rather naively perhaps, that a fundamental kind of

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strength underlies the resistance of metals to all kinds of loads. This fundamental kind of strength is the ultimate tensile strength and represents simply the resistance a bar of the material will have (expressed in pounds per square inch of cross section) to being pulled apart in the direction of its length. With this value at his disposal and with the aid of some moments of inertia, some empirical values of Young's modulus and Poisson's ratio, and a dash of calculus, the clever engineer will determine the resistance that any kind of structure, from a springing board to the crankshaft of an automobile, will offer to any kind of load that may be applied. If he is wise, he covers the inaccuracies of his assumptions with a generous factor of safety.

Strangely enough, however, the tensile test does yield more valuable information about the material than any other single test. Moreover, there seems to be correlation, or proportionality, between ultimate tensile strength and certain other values such as hardness and fatigue limit. This seems all the more remarkable when we consider the true meaning of ultimate tensile strength and the method of its determination.

The Tensile Test

This test consists briefly of measuring the force required to pull a bar of the material apart. A standard bar [1] is 0.505 inch in diameter, representing a cross-sectional area customarily treated as 0.2 square
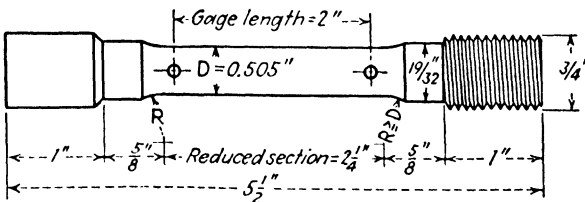
FIGURE 15.1. A standard tensile test specimen.

inch (more precisely, 0.2003 square inch). The actual shape is shown in Figure 15.1. The ends may be threaded or smooth, depending upon the kind of machine and grips used to pull the test.

It is beyond the scope of this book to describe all the sizes and shapes of test specimens or the machines used for pulling these tests. Suffice it to say that the ends of the piece are fastened in the grips

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[1] The standard British test bar has a diameter of 0.564 inch, representing a cross-sectional area of about 0.25 square inch, with a 2-inch gage length. The metric-system bars used in Germany were 1 centimeter in diameter with 10 centimeters gage length, and 2 centimeters in diameter with 20 centimeters gage length.

of the machine which are then slowly pulled apart. The force required to do this is determined at all times.

The maximum number of pounds of force required in breaking the piece divided by the *original* cross-sectional area is called the *ultimate tensile strength*. The value is given in pounds per square inch. Of course this is based on the assumption that the force required to break an actual square-inch section would be proportional to that required to break the 0.2003-square-inch section. (*Note*. Tungsten wires show a wide variation in this matter.)

Percentage of Elongation

While the ultimate tensile strength is being determined, a number of other values can be measured. Metals stretch somewhat before they break. Different metals stretch differently so a measure of this stretch is of value in qualifying the metal. Two punch marks are made on the side of the test piece 2 inches apart; this is called the gage length. After the piece is broken the two parts are placed in contact at the fracture, and the distance between the punch marks is measured. The difference between this measurement and the original 2 inches is the amount the piece has elongated or stretched. This value, divided by 2 (the original length) and multiplied by 100, is recorded as *per cent elongation in 2 inches.*

It is always necessary to record the original gage length with per cent elongation because the piece does not elongate uniformly along its length. In the vicinity of the fracture it is found to be elongated

FIGURE 15.2.   Necking down.

more than at other points so that the greater the gage length the lower will be the value for per cent elongation. This elongation is associated with what is termed "necking down"; as the piece elongates it becomes thinner, that is, smaller in section. In ductile materials the effect becomes greatest at some one place along the bar. The thinner the bar becomes at that place, the less is its reduced area of section able to sustain the load so that the neck is the place where fracture ultimately occurs. (Figure 15.2.)

Percentage of Reduction of Area

The diameter of the necked down portion is measured after fracture occurs and the area of section calculated. The difference between

this value and the original 0.2003-square-inch [2] section is the amount the area has been reduced. The reduction of area is calculated to per cent of original section, again assuming that the size of the piece does not make any difference.

It must not be assumed that the elongation and reduction of area take place gradually as the load is applied. Since they are both meas-
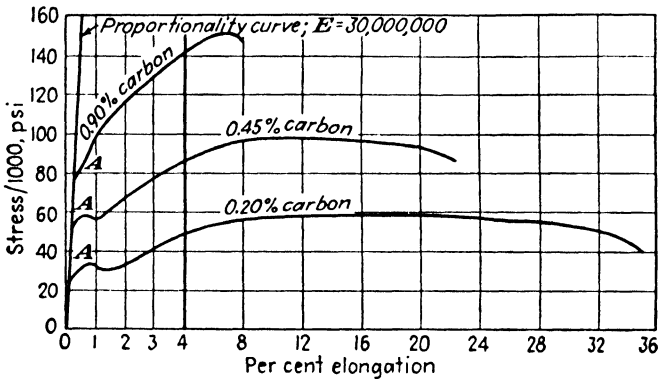
FIGURE 15.3. Typical stress-strain diagram.

ured after the piece has broken and the load therefore has been re-leased, they represent a permanent change in the shape of the piece. This permanent change does not start to take place until the load has reached a high value; in the case of soft steel about half the ultimate strength. Below this load the piece stretches elastically, in accordance with Young's modulus, but returns to its original dimensions if the load is released. Stress-strain diagrams serve to illustrate the relation of stretch to load. (Figure 15.3.)

Elastic Limit and Yield Strength

These curves are obtained by using an extensometer which indicates and magnifies the elongation throughout the test. The lower portion of each curve, up to the point where it deviates from a straight line, represents the elastic stretch. The load at which it starts to deviate is the *elastic limit*. This is frequently difficult to determine exactly. The point A in the mild steel diagram is termed the *yield strength*. Here the piece suddenly stretches so rapidly that the load required actually may drop to less than its previous value. The yield point is easily determined while observing the test, even without an exten-someter, and is consequently usually recorded as one of the items

[2] Usually calculated as exactly 0.2000 square inch.

of the tensile test. It is higher than the elastic limit and does not have as much significance.

Proof Stress. Low-carbon irons and annealed steels show definite yield points. Most other metals do not, but a value is frequently determined that is known as the proof stress. This is the stress that will produce an elongation of arbitrary value, usually 1 or 2%. The value is placed high enough to exceed any possible elastic stretch and yet small enough to be indicative of the beginning of permanent deformation.

We have then the following tensile test items:

1. Ultimate tensile strength in pounds per square inch (psi).
2. Yield strength in pounds per square inch (psi).
3. Elongation (elong.) per cent in 2 inches.
4. Reduction of area (RA) per cent.

Table 1 may serve to illustrate the results of tensile tests.

TABLE 1

Material	Tensile strength, psi	Yield strength, psi	Elongation, per cent in 2 in.	Reduction of area, per cent
Ingot iron (annealed)........	41,000	18,300	47.0	70.6
0.45% C steel (annealed)....	89,000	50,000	29.0	48.0
Cr-Ni steel, SAE 3240 (annealed)...............	132,000	116,000	21.0	60.0
Stainless steel (18% Cr–8% Ni)	90,000	32,500	57.5	72.5
Copper................ ...	31,700		58.0 *	72.8
High brass................	53,000		54.0	

* Gage length for pure copper is $4\sqrt{A}$; A = area of cross section.

Uses and Limitations of the Tensile Values

The results of the tensile test are the most frequently used values in the design of structures, however imperfectly they describe the behavior of the metal in the structure. Consider, for example, the ultimate tensile strength as determined on a test piece and as actually existing in a square tension member. It may be taken as axiomatic and has been pointed out by James Thompson (1875) that "Similar bodies of homogeneous material are alike . . . strained . . . by loads proportional to their linear dimensions provided these loads are applied in the same manner and are similarly distributed." This would indicate that the strength of a large piece is proportional to the strength of a small

piece provided the two were the same shape and necked down in the same manner and provided the material was homogeneous. These last two statements might be open to question, however, even in a round bar, and of course between a round and a square section there is no similarity of shape.

In the case of sheets, plates, and odd sections it is not always possible to get a test of the standard shape described above, so pieces are cut out to rectangular section or whatever is most convenient. Sometimes a piece of the entire bar may be used as a test piece, for instance a small pipe, a small angle or channel, or a wire. When the part in the grips of the machine is no larger than the section in the gage length, the results must be taken as somewhat inexact.

Young's Modulus

Below the true elastic limit metals stretch an amount that is proportional to the stress applied. This means that the load divided by the stretch equals a number that is the same for all loads up to the elastic limit. If we express the load in pounds per square inch of section, and the stretch in inches per inch of gage length we get

$$\text{Young's modulus} = \frac{\text{stress}}{\text{strain}} = \frac{\text{pounds per square inch}}{\text{inches per inch}}.$$

This value is surprisingly constant for any one kind of metal. For carbon steels and the low-alloy steels, it is always between 29,000,000 and 30,000,000 psi (inch-pounds per inch cubed).

In the design of structures metals must never be stressed beyond the elastic limit. This makes it comparatively easy to calculate the amount the metal will stretch under the load applied. Young's modulus is also called the modulus of elasticity.

Poisson's Ratio

When a bar is pulled in tension within the elastic limit, it elongates in the direction of the pull and becomes somewhat reduced in section and diameter. The ratio of the change in diameter per unit diameter to the change in length per unit length is Poisson's ratio.

Poisson's ratio enters many design calculations. It varies for different metals. For structural steels it is roughly placed at 0.25, although it usually runs a little higher (0.28). It is an indication of the amount of stretching of atomic distances and also indicates that there is a volume change. Metal under tension is less dense than when the tension is released. If there were no change in volume, Poisson's ratio would be 0.50.

Hardness and Hardness Testing

One of the simplest concepts regarding the physical properties of metals ·is that of hardness. Lead is soft, and steel is hard. Quenched steel is harder than annealed steel. Cold-worked metals are harder than cast metals of the same kind. The idea of hardness may be applied to all substances whether metallic or not. Oak is hard; pine is soft; rocks are hard; flesh is soft.

Hardness, like many elementary and primitive concepts, is difficult to define. A rational scale by which to measure hardness is not easy to select. A consideration of some of the factors involved in the idea of hardness may help to explain this difficulty.

1. Hard substances do not break easily.
2. They are not easily dented.
3. They are not easily scratched.
4. They do not wear away rapidly by abrasion.

On the other hand,

5. Hard substances may be used to fracture other substances.
6. They produce dents in softer materials against which they are pressed.
7. They will scratch softer materials.
8. In finely divided form they make good abrasives.

Some of the above statements are only partly true, as for instance the first and fifth, because a substance might be quite hard and yet so brittle as to break easily. Quartz, for instance, is hard as steel yet is quite fragile. Other statements conflict in many cases; a piece of chalk can easily deform soft rubber and yet will make a mark upon it by abrasion of the chalk.

Mineral Hardness

Scratching and abrasion are of course quite similar and have led to the scale of hardness known as Mohs' scale. This arbitrarily classifies all substances as to hardness on the basis of whether they will scratch or be scratched by ten standard substances. These standard substances are classified in order of hardness as shown in Table 2.

To determine the hardness of a substance on this scale it is merely necessary to find, by trial, which mineral will scratch a smooth surface on the substance and which mineral can be scratched by the substance. The hardness of the substance lies between those of the two minerals.

Of course this test does not give a very fine distinction between sub-

TABLE 2. Mohs' scale of hardness

Hardness no.	Mineral	Characteristic chemical formula
1	Talc	$H_2O \cdot 3MgO \cdot 4SiO_2$
2	Gypsum	$CaSO_4 \cdot 2H_2O$
3	Calcite	$CaCO_3$
4	Fluorite	CaF_2
5	Apatite	$CaClF \cdot 9CaO \cdot 3P_2O_6$
6	Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
7	Quartz	SiO_2 (hexagonal)
8	Topaz	$Al_2F_2O_2 \cdot SiO_2$
9	Corundum	Al_2O_3
10	Diamond	C

stances in which the hardness variation is small. All the steels would lie between 5½ and 8 on such a scale. Moreover, when similar substances whose hardnesses are quite close together are tested by this method, each substance will scratch the other and the result becomes indeterminate.

Indentation Hardness

The other criterion of hardness that is commonly used is indentation. This is much more satisfactory for metal testing because quantitative values can be obtained that vary by steps as small as we please and because the results can often be correlated with other physical properties. Indentation hardness and tensile strength, for instance, are roughly proportional for materials of like texture, for example, annealed carbon steels.

Briefly, indentation hardness tests comprise first, those in which the size of the indentation is measured when the indentation is produced by a fixed load; secondly, those in which the load required to produce an indentation of given size is measured; and thirdly, those that measure the effect of the indentation in reducing the rebound of an indenter that strikes the specimen at a given velocity. Obviously, indentation tests may be used only on materials that are plastic enough to be dented without breaking.

A large number of indentation hardness-testing devices have been invented. A few of these have found wide commercial application and will be described.

The Brinell Hardness Test

This consists of a hydraulic press, the piston of which is supported by a ball that rests on the surface to be tested. The ball is made of

hardened steel and, in the original design, is a centimeter in diameter. Loads as high as 5000 kilograms (11,023 pounds) can be applied by the press. The standard load, however, is 3000 kilograms (6614 pounds). For softer materials loads as low as 500 kilograms (1102 pounds) may be used. The load is maintained at its maximum value for thirty seconds. The original Swedish design is shown in Figure 15.4.

A number of other designs are on the market. They all accomplish the same purpose, however, namely, forcing a ball of standard size against the specimen under a fixed load.

After the impression is made the specimen is removed from the machine and the diameter of the circular impression is measured by means of a microscope with a micrometer eyepiece. The Brinell hardness number (BHN) is then calculated by the formula [3]

$$ \text{BHN} = \frac{P}{A} = \frac{P}{\frac{\pi D}{2}(D - \sqrt{D^2 - d^2})}, $$

where P = the load in kilograms;

A = the spherical area of the impression;

D = the diameter of the steel ball in millimeters (10 mm);

d = the diameter of the impression.

From this it can be seen that the Brinell hardness number is equal to the pressure, in kilograms per square millimeter, that the specimen will support under the conditions of the test.

We shall see later that it is wrongly assumed that D of the formula is the same as the diameter of the steel ball. This and other inexactitudes make the Brinell test imperfect from a theoretical standpoint. However, it gives highly reproducible results and has won great favor as a means of evaluating this important property of metals.

[3] Spherical area, in the equation for Brinell hardness, may be calculated as follows (see diagram):

$$ ds = \frac{D}{2} d\theta $$

$$ x = \frac{D}{2} \sin \theta $$

$$ \text{area} = \frac{\pi D^2}{2} \int_{\cos \theta - 1}^{\cos \theta - \sqrt{\frac{D^2 - d^2}{D^2}}} \sin \theta \, d\theta $$

$$ = \frac{\pi D}{2}(D - \sqrt{D^2 - d^2}) $$
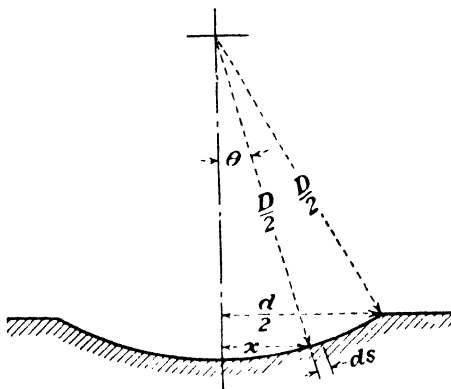
The Rockwell Hardness Test

Like the Brinell method, the Rockwell hardness test consists in measuring the size of an impression produced by forcing an indenter into the surface of the specimen under a fixed load. The indenter may be either a steel ball or a carefully ground diamond cone. Two sizes of balls are used, $\frac{1}{16}$ inch and $\frac{1}{8}$ inch. The diamond cone is ground
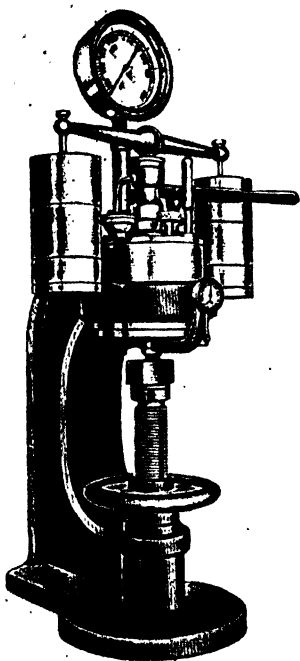
FIGURE. 15.4. Brinell hardness-testing machine (*Burrell Technical Supply Co.*).
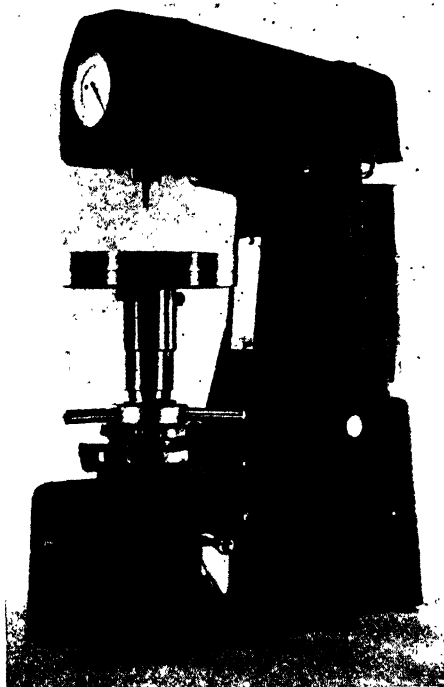
FIGURE 15.5. Rockwell hardness-testing machine (*Wilson Mechanical Instrument Co.*).

to an angle of 120°. Much smaller loads are used in the Rockwell than in the Brinell test and the impressions produced are much smaller.

In any case the Rockwell machine measures the depth of the impression rather than the diameter. This measurement is read on the dial of a micrometer depth gage that is connected to the indenter so that no microscope is used.

The dial is divided into 100 divisions which are numbered backwards so that the greater the depth the less the reading. The units of depth are arbitrary as is the Rockwell hardness number itself. Actually, the *Rockwell hardness number* is the *difference between the depth*

of the impression, in arbitrary units, and an arbitrarily assumed maximum possible depth that represents 100 divisions on the scale.
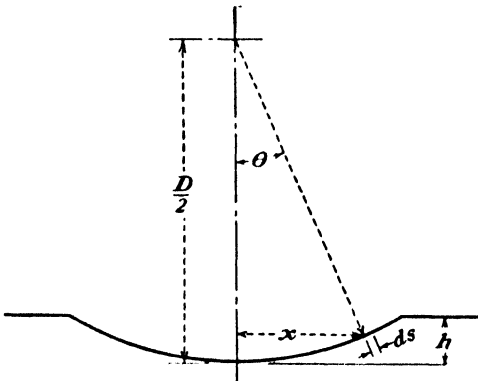
In making the Rockwell test the specimen is supported by the anvil (or pedestal) of the machine which is forced upward by a jack screw until the specimen comes in contact with the indenter raising it slightly and, in so doing, supporting the various loose parts of the depth gage and machine. The hand of the depth gage turns backward about three revolutions. This, of course, introduces a small load on the indenter which is called the minor load. The machine is designed so that this minor load is 10 kilograms. Then, by releasing a system of levers, an additional load is added which forces the indenter down into the surface of the specimen. The additional load is chosen for the particular type of material being tested and varies from 15 to 150 kilograms. Before the reading of the gage is taken the major load is removed, leaving the indenter in the new position but only under the minor load of 10 kilograms.

It is claimed for the Rockwell hardness test that it eliminates uncertainties in measurement which occur in the Brinell test, in which, it is pointed out, the true edge of the shallow spherical impression is not clearly defined. The smaller impression is an advantage on small or thin specimens. By the use of the diamond-pointed indenter much harder materials can be tested.[4]

Correlation of Brinell and Rockwell

It would seem, on first consideration, that we might easily calculate the Brinell hardness from the results of the Rockwell if we knew the exact depth of impression in millimeters and the load. In this case,

[4] Calculation of spherical area from depth of impression:

$$ds = \frac{D}{2} \, d\theta$$

$$x = \frac{D}{2} \sin \theta$$

$$\text{area} = \frac{\pi D^2}{2} \int_{\cos\theta\,=\,1}^{\cos\theta\,=\,\frac{D-2h}{D}} \sin\theta \, d\theta$$

$$= \pi D h$$

for instance, the spherical area of the impression, calculated from the depth, is equal to πDh, where h is the actual depth of the impression in millimeters and D is the diameter of the ball in millimeters. Now if we convert the values we get for Rockwell reading into Brinell units we might consider that

$$\frac{P}{A} = \frac{P - p}{\pi Dh}$$

should equal the Brinell number, P being the major and p being the minor loads in kilograms, and D and h expressed in millimeters. This would only be true, however, if the balls for both Brinell and Rockwell tests were ideally rigid, or non-compressible, and the material tested were perfectly plastic and did not recover from the strain at all. Actually, however, the indenting balls always compress a little, leaving an impression whose radius is greater than the $D/2$ of the ball; how much greater will depend upon the actual load and the modulus of elasticity (Young's modulus) of the material tested.

These effects are by no means negligible and simply mean that there is no calculable correlation between the two methods of testing hardness. The best that can be done is by tables of comparative values obtained experimentally on a variety of substances. Such tables are offered with no guarantee as to accuracy by some of the manufacturers of hardness-testing machines.

The Vickers Hardness Test

This is very similar to the Brinell in that an impression is made by an indenter and the dimensions of the impression are then measured with a microscope. In the Vickers machine the indenter is a diamond
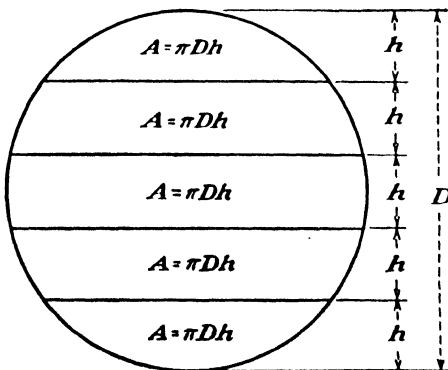
Since the equation is linear, h may be taken as the difference in depth between major and minor loads, that is, the thickness of a spherical segment.

pyramid having four sides.[5] The angle between opposite sides is 136°. This gives an indentation that appears as a dark square. The diagonals of the square are measured and the area of the pyramidal surface is calculated. The hardness number is the total load divided by this area.

The area of the pyramidal surface for a 136° pyramid equals $d^2/1.8544$ where d is the diagonal measured. The hardness H is then easily determined from the relation,

$$H = \frac{\text{load}}{\text{area}} = \frac{1.8544L}{d^2}.$$

Up to a hardness number of about 300 the Vickers and Brinell values are practically identical. At higher values the Brinell gives lower results than the Vickers. Brinell values are not reliable above 600 whereas with the Vickers diamond pyramid, results up to 900 may be obtained.

The Vickers hardness testing machine is handsomely constructed. The load is applied automatically in a manner similar to the Rockwell machine, but after the correct time it is automatically released. The specimen is removed from under the indenter and a microscope and illuminating lamp are swung into exact position for measuring the diagonal of the impression. This measurement is made by adjusting

[5] Calculation of pyramidal surface from the diagonal d:

h = altitude of a triangular face of the pyramid

$$= \frac{d}{2\sqrt{2} \cdot \sin \frac{\theta}{2}}.$$

Area (of 4 triangular faces) $= 4 \frac{hd}{2\sqrt{2}} = \frac{d^2}{2 \sin \frac{\theta}{2}}.$

For $\theta = 136°$,

$$\text{area} = \frac{d^2}{1.8544}.$$
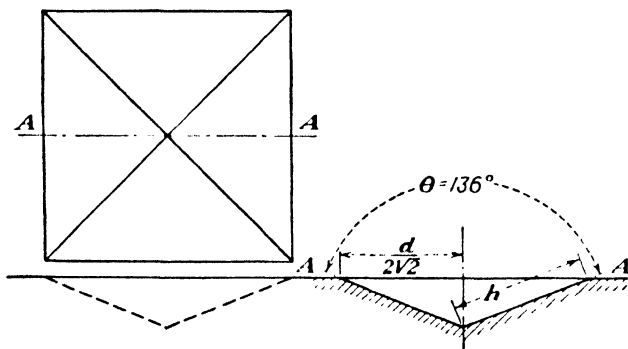
the position of two knife edges, in the field of view of the microscope, until they touch opposite corners of the square impression. The micrometer screw by which the knife edges are moved carries the scale that measures their distance apart so that the actual measurement is read from this screw and not through the microscope as in the Brinell. The loads used vary from 5 to 150 kilograms so that the impressions are small.

The chief advantage claimed for this method is that by measuring the diagonals of a square pyramidal impression, difficulties due to

FIGURE 15.6.   Sinking in and piling up of edge of impression. Left, impression rounded downward; right, impression piled up.

rounding the edges of the impression are eliminated. It is claimed that the corners of the square impression are sharp and neither rounded downward nor piled up, either of which condition may occur with a spherical impression.

The automatic timing, the small-sized impression, the accurate method of reading the diagonal of the impression, and the constancy of shape of the impression produced by the pyramidal diamond indenting tool are also listed as advantages.

Although the values obtained by this test are practically independent of the load, due to the similarity in shape of all impressions, the fundamental accuracy of the test, as applied to different substances, may be open to question. This is due to piling up or sinking in along the edges of the impression. Some materials tend to pile up, others to sink in. Theoretically, the corner measurements would give hardness values that are too high for metals that tend to pile up and too low for those that tend to sink in.

The Shore Scleroscope

The Shore scleroscope is entirely different in principle from the machines just described and, briefly, measures the rebound of a weight that is dropped onto the specimen. The machine consists essentially of an anvil or firm rest on which the specimen is placed; a vertical glass tube about 10 inches long, the lower end of which rests on the surface to be tested; and a small cylindrical weight that drops through the tube onto the surface of the specimen from which it rebounds upward. A scale back of the tube enables the operator to estimate the height of the rebound. At the top is a mechanism for releasing the

weight which is actuated by squeezing a rubber bulb similar to an atomizer bulb.

The weight weighs 2½ grams and is provided with a bluntly pointed diamond at the bottom. This furnishes a hard, unyielding surface of contact between the weight and the surface to be tested. For some purposes a hardened steel ball 3 millimeters in diameter is substituted for the diamond.

The effect of dropping the weight upon the specimen is to indent the specimen slightly. This does work on the specimen and consequently absorbs energy from the weight so that it does not bounce up as far as if no energy were absorbed. The harder the specimen, the less it is indented and the higher the rebound. The scale is purely arbitrary, 100 divisions being a little higher than the rebound from the hardest steels.

Advantages of the method are the very small impression which is almost unnoticeable even on polished surfaces, and the rapidity of the test. However, it requires considerable practice to estimate the height of the rebound accurately, and usually several tests must be made on one specimen before a satisfactory result is obtained. To obtain a correct result, the vision should be directed to very nearly the point of maximum rebound.

A recording modification of the scleroscope is the model D, which uses a longer and heavier weight, dropping through a shorter distance so that the striking energy is the same as the other (Universal C–1 model). In the model D the rebounding weight is caught by a clutch at its maximum rise. From there it is moved up to its starting position in contact with the dial mechanism which records the height of the rebound. It is not considered quite so accurate as the other model.

Other Hardness Tests

The tests described above are probably the most used of all the various methods. Many others are in use, however. Mention should be made of the *Monotron* hardness test, which measures the pressure required to force an indenter into the specimen to a standard depth; also, the *Cloudburst* test which showers hardened steel balls on the surface to be tested and determines the height from which they must be dropped to just show indenting effects. Other effects may be determined, such as the diameters of the impressions when the balls fall from a standard distance, higher, of course, than in the first case.

The Bierbaum Microcharacter

In this test the technician measures the width of a very fine scratch produced by drawing a specially prepared diamond point across the

polished, or polished and etched, surface of the specimen, under constant load. The load used may be either 3 grams or 9 grams, and the width of the very fine scratch must be measured microscopically at magnifications in the neighborhood of 2000 diameters. If the 3-gram load is used, the hardness number equals 10,000 divided by the square of the width of the scratch in microns. If the 9-gram load is used, the result of this computation is multiplied by 4 to get the hardness number.

Although the results are not comparable to those obtained by other methods, it is an excellent means of determining the *relative* hardness of microconstituents and of finely divided phases.

The Knoop Hardness Test

This is another that is used to determine the hardness of minute structural features. Like the Brinell, Rockwell, and Vickers tests, it is a pressure-indentation test and its results can to some extent be correlated with theirs. It uses a diamond point indenter that is ground to a four-sided pyramid, but with one diagonal of the base of the pyramid much longer than the other. This produces a diamond-shaped indentation, and measurements are made microscopically on both the long and short diagonals of the impression. Loads as low as 100 grams can be used so that the impressions can be made small enough to lie within the areas of some microconstituents. The instrument is so arranged that the operator can select, microscopically, the exact location for the indentation.

The Herbert Pendulum Tester

This device determines a number of values related to the hardness of the specimen, including work hardenability. It consists of a cast metal arch, supported at its middle, on the specimen, by a 1-millimeter ball. In this position the arch can be swung back and forth like a pendulum. The size of the indentation, the way the pendulum responds to swinging, and the angle at which it comes to rest are all recorded and furnish information regarding the character of the specimen.

File

Finally, an excellent way to estimate hardness for comparative purposes is by scratching the specimen with a clean, unworn file. Many mistakes in the selection of metals in the machine shop can be avoided by this simple test in the hands of an experienced mechanic. Soft spots in tools, poorly heat-treated articles, and wrongly labeled stock can frequently be detected by this method.

Impact Testing

The tensile and hardness tests are used to determine what are commonly called static characteristics of the material. The loads are usually applied slowly so that the test piece may be considered to be in equilibrium with the load at all times. Such tests foretell the behavior of the metal in structures that are subjected to fixed, unchanging loads, or if the loads do change, they do so slowly and infrequently. In these days of rapidly moving machinery, however, the results of such static tests are found to be quite erroneous when applied to parts subjected to rapidly changing or reversing stresses, and to sudden stresses or shock. Much study and effort have been spent in trying to devise suitable tests to qualify materials with respect to these new requirements, and the problem is as yet only partly solved.

A test for resistance to suddenly applied loads is particularly troublesome to devise. Manifestly, the ordinary tensile test could not be applied with sufficient rapidity because of the inertia of the parts of the machine. For very rapid stresses, the impact test utilizes this inertia rather than trying to dispense with it. All forms of the impact test depend upon a swinging pendulum. The height from which it drops is a measure of its inertia at the lowest point. There it collides with the specimen, breaking the latter, and continuing onward in its swing. The height to which the pendulum rises is dependent upon the inertia left in it after breaking the specimen; and the difference between this height and the height to which it would have risen, had no specimen been present, is a measure of the energy required to break the specimen. This, expressed in foot-pounds, is the impact value of the specimen.

There are two commonly used types of impact test machines, namely, the Charpy and the Izod. Both utilize the principle stated above. The differences are in the design of the test piece and the method of supporting and striking it.

In the Charpy test the specimen is supported at its ends, and the pendulum bob strikes it midway between the supports. In the Izod test the specimen is supported in a vertical position as a cantilever, the lower end being gripped in a vise. The standard Charpy test bar is 5.5 centimeters long and of square section, 1 centimeter on a side. The Izod test bar is 7.5 centimeters long and the same as the Charpy in section.

For most ferrous metals and all of the softer metals, the test bar has a notch, or groove, cut across the tension side. This locates the point of fracture and gives lower results than would be obtained on

the unnotched bar. The effect of the notch is so great that much care and accuracy is necessary in cutting it. The depth and curvature at the base of the notch should be correct to about a ten thousandth of an inch.

The striking velocity in the Charpy machine is 17.39 feet per second and the capacity is 217 foot-pounds (30 kilogram-meters). This requires a drop of nearly 5 feet and a pendulum weight of over 45 pounds. In the Izod machine the striking velocity is 11.48 feet per second and the capacity is 120 foot-pounds.

While the results of the tests are expressed in foot-pounds there is not much correlation to be found, either between the different types of impact test, or with other physical tests. A high impact value indicates better ability to withstand shock than a low impact value, but if we know the Charpy impact value of an automobile axle steel we cannot depend upon it as a quantitative guide in the design of the axle.

Fatigue and Fatigue Testing

Metals subjected to reversed or repeated stresses fail at loads that are far below their ultimate tensile or compressive strengths. We are acquainted with the method of breaking a wire by bending it back and forth a number of times, but there of course we are exceeding the yield point, which is never done in the design even of stationary structures. We feel the wire get hot as we bend it and realize that changes are taking place within the metal. But if they had been repeated often enough the wire would have broken even at much lower stresses—stresses below the yield point.

Driving in our automobile, we leisurely change gears with no unusual jar or suddenness. The engine races as we apply the accelerator, and the car slows down and stops, if we are lucky enough not to be on a hill. Examination reveals that the driveshaft or axle is broken squarely in two. The fracture is very smooth, almost polished, and we are told by the mechanic at the repair shop that the metal "crystallized." Just why this metal should suddenly crystallize at a temperature 500° below that at which any crystalline changes were ever observed microscopically is not clear, but that is his story.

As a matter of fact, if the metal had crystallized, as metals do when annealed, the axle would not have broken. The failure was a case of fatigue. Fatigue, for lack of a better term, describes a cause of failure in metals that are subjected to many reversed or repeated stresses below the ordinarily accepted elastic limit (yield point). Unusual cases of fatigue may have originated in small cracks, dents, or scratches in

the surface of the piece. Such defects are enlarged at each application of the stress, and the faces of the fracture are pressed smooth at each reversal. However, even in the absence of defects, all metals will fail in the above manner if the load is high enough and the number of reversals of stress great enough.

Many tests have been devised to determine the ability of a metal to withstand fatigue. A description of one frequently used method should suffice to illustrate the principles involved. The test is known as the rotating beam test. The machine used today is essentially a development and refinement of that used by A. Wöhler, whose results were published in *Zeitschrift für Bauwesen* between 1858 and 1870.

Figure 15.7 shows diagrammatically the arrangement of the Wöhler machine. The test beam is supported on ball bearings, and the load is applied through ball bearings, the loads at B and C being equal. The distances AB and CD also are equal. This produces a uniform bending moment over the length BC. The beam is reduced in section at the middle so as to locate the fracture there. The revolution counter is placed at the opposite end of the beam from the drive. Thus, when the beam breaks, the counter stops and records the total number of revolutions.

Each revolution of the beam produces a complete reversal of stress in the beam. In order to avoid excessive stresses due to inertia of imperfectly centered parts, the speed should not exceed 2000 rpm. Each test determines the number of revolutions required to break the specimen under the load used. From the actual load is calculated the skin stress, from the usual formula for a beam of circular section loaded as indicated. From the skin stress may be calculated the *unit stress* in pounds per square inch of section.[6]

The information derived from a single test of this kind is of very limited application. If, for instance, a specimen under a unit stress of 20,000 psi breaks in ten thousand revolutions, it tells us only that we must use a lower unit stress on such materials if they are to be used under dynamic loads. But it does not tell us how much lower. For such parts as motor and engine shafts, axles, and connecting rods, we would like to determine the limiting stress under which the piece would never break, no matter how many reversals occurred.

That such a limiting stress exists is pretty certain, for some metals at least, but it must be determined by a considerable number of

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[6] For a circular section of diameter d, the stress in extreme fibers (skin stress) is equal to $16Wa/(\pi d^3)$; a is distance between point of support and point of application of the load on either side, and W is the total load. The weight of the test piece is, of course, neglected.
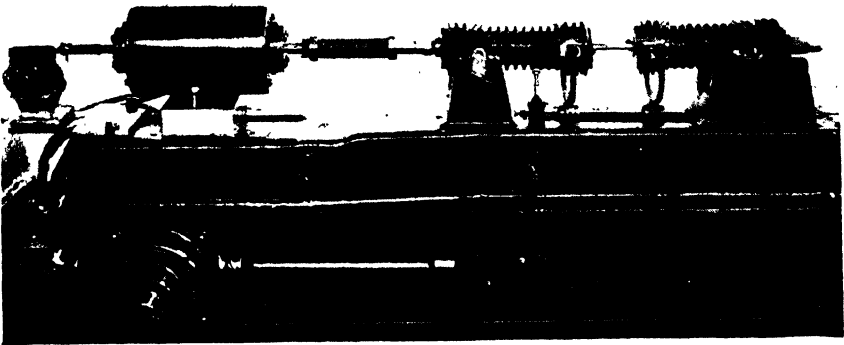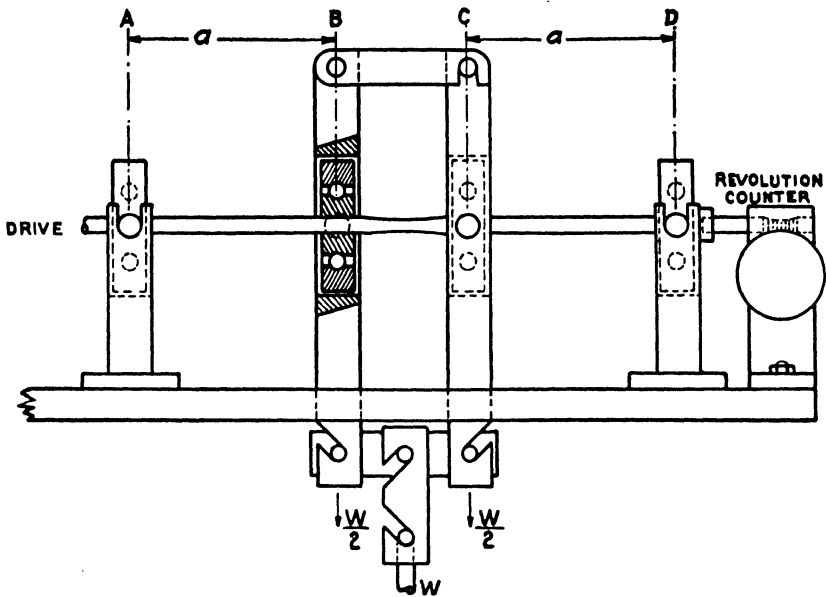
FIGURE 15.7. Diagram of the Wöhler rotating-beam fatigue-testing machine (Farmer type) and photo of a modern machine employing the same principles. (Diagram redrawn and simplified from H. F. Moore and J. B. Kommers, *Bulletin 124*, University of Illinois Experiment Station, October 24, 1921.)

fatigue tests. It is found that as the stresses used in successive tests are lowered progressively below the yield point, the number of revolutions required to break the piece increases rapidly. A stress is finally found, which for ordinary carbon steels is about two-thirds of the yield-point stress, under which many hundreds of millions of
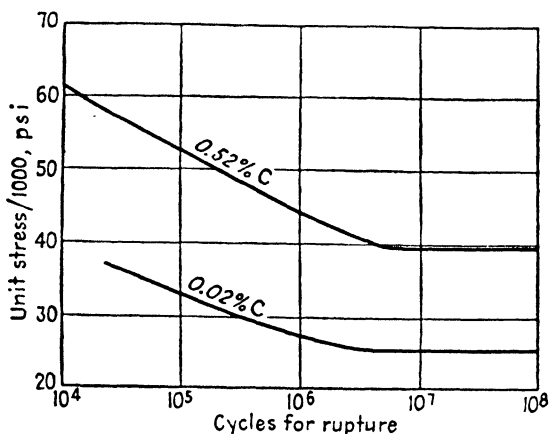
FIGURE 15.8. Typical fatigue limit curves for normalized steel (semi-logarithmic) (redrawn and simplified from H. F. Moore and J. B. Kommers, *Bulletin 124*, University of Illinois Experiment Station, October 24, 1921).

reversals will not break the piece. But it is also found, by plotting number of revolutions required to cause failure against the stress used, that when the piece does not fail in ten million reversals it will never fail. This is illustrated in Figure 15.8.

The value ten million is for carbon steels. Other values have been determined for other metals. The original determination of these values was, of course, very tedious since the tests had to be run for long periods of time. At 2000 rpm [7] it takes about three and one-half days to run ten million revolutions and some of the earlier tests were run for hundreds of millions of revolutions. After this value is determined, however, it is only necessary to find the stress the material will withstand for ten million reversals.

The fatigue limit, then, is the maximum unit skin stress the material will withstand for a sufficient number of reversals to prove that it will withstand it indefinitely, in the case of steel ten million reversals. Even this is a tedious test requiring at least four or five expensive determinations (for some materials many more), and much effort has been spent in trying to devise shorter tests that will yield the same

[7] Modern machines have considerably higher speeds.

information. These tests make use of such devices as varying the load at intervals after the test has started. The results are not strictly comparable to the regular test, however, and are likely to be badly misleading.

The above is an outline of the phases of physical testing that are of most interest to the metallurgist. Innumerable other tests might be dealt with such as bend tests, drop tests, shear, tension, and compression tests, high-temperature tests, creep tests, corrosion fatigue, and repeated impact, all of which could furnish material for an encyclopedia of physical testing. Almost every branch of the metals industry has, in addition to the tests outlined above, one or more special tests for some particular material or product. Attempts to standardize and correlate many of these tests will be found described in the publications of the Society of Automotive Engineers (SAE) and the American Society for Testing Materials (ASTM).

SOME REMARKS ON THE PLAN OF THIS BOOK

The text, up to this point, has sought to acquaint the student with some fundamentals of metal chemistry, phase equilibria, crystallography, and heat treatment of metal alloys. Slight mention has been made of specific useful alloys and then only when such mention might aid in presenting the above principles. This work has been used by the author as the basis for a college course of one quarter (about twelve weeks).

The remainder of the text deals more specifically with systems of practical useful alloys. The attempt is made to apply the principles now learned and to utilize them as far as possible in the explanation of the actual processes and treatments that comprise alloy technology.

Chapter XV covers material that might well have been studied in courses in physics or mechanics; but it has been introduced at this time for those who are not prepared in these subjects, or as a review for the students who may have forgotten many of their details. Increasing reference will be made to the terms and methods described herein in the chapters to follow.

Since Chapter XV deals with material somewhat foreign to the natural domain of the text it is not supplemented with problems and questions.

The Chemistry of the Carburizing Process and Controlled Furnace Atmospheres

Description and Purposes of Carburizing · Pack Carburizing · Chemistry of Pack Carburizing · Intensity and Depth of Carburization · Mechanism of Pack Carburizing · Gas Carburizing · Chemistry of Gas Carburizing · Equilibria in Furnace Atmospheres

As a special heat treatment, case carburizing affects the structure of steel. Strictly speaking it creates no structures that have not already been discussed. However, it throws much light on the way steel structures are formed and because of its industrial importance, could scarcely be omitted from a comprehensive discussion of steels.

Description and Purposes of Carburizing

The process is essentially that of adding carbon to the surfaces of steel articles by heating them in carbonaceous surroundings. These surroundings may be solid, liquid, or gaseous. The temperature is such that the steel is in the austenitic condition, that is, between A_3 and the delta iron range (A_4). At this temperature the steel can absorb carbon from such surroundings, the carbon penetrating the surface and becoming part of the austenite in a zone that extends inward from the surface. As time proceeds the zone becomes thicker, due to diffusion inward.

The effect of carburization and subsequent heat treatment is to produce a hard, strong, or wear-resistant surface on an otherwise soft,

ductile, or tough piece of steel. The purposes and reasons for doing this are really quite varied. In many cases it offers an easy solution to problems in machining and heat-treating of intricate shapes that would be extremely difficult to handle if high-carbon steels were used. Gears, for instance, can be machined from mild steel blanks and then carburized to give strong, wear-resisting surfaces to the teeth. In other cases the combination of a hard exterior with a tough but ductile interior is thought to fortify the piece against destruction to a greater degree than can be attained in steel of uniform composition. A very useful test for hardening and other characteristics of various steels (the McQuaid-Ehn test) depends on a study of the carburized zones in specimens of the steels.

The carburized portion of the piece is known as the *case* while the center portion in which the carbon content has not been increased perceptibly is the *core*. Cases vary in thickness from less than a thousandth of an inch to more than a quarter of an inch. In fact, armor plate may be carburized to a depth of an inch or more.

The carburizing processes are divided into three distinct categories, viz., pack carburizing, gas carburizing, and cyaniding or liquid-bath carburizing. In pack carburizing the steel is surrounded by some form of charcoal (animal or vegetable) to which has been added, usually, some inorganic material such as $BaCO_3$. In gas carburizing the steel is surrounded by some carbon-containing reducing gas, which may be either CO or hydrocarbons, such as CH_4, or both. Cyaniding and related treatments consist in immersing the steel in molten baths of sodium or potassium cyanide more or less diluted with inert salts such as NaCl or Na_2CO_3.

Pack Carburizing

Pack carburizing is probably the oldest method and dates back to the old cementation process in which steel was made by heating wrought iron in a suitable charcoal mixture until the pieces were carburized or "cemented" throughout.[1] In the earlier applications of the process little was known of the chemistry involved, and much secrecy surrounded the recipes for carburizing mixtures, many of which were long and involved.

[1] A few plants are still said to operate that make "cemented" steel. A later development remelted the cemented steel in crucibles and cast it into ingots which were rolled into bars. This was the original crucible process that produced an extremely high-grade product which went by the name "cast steel." Later, manufacturers who produced household articles from rolled Bessemer and open-hearth steel and even from steel castings succumbed to the temptation to label their product "cast steel" to give the impression that it was this high-grade crucible product. Nowadays, the name applies only to steel castings.

Research by the Italian metallurgist Giolitti[2] in the early part of this century did much to put the process on a scientific basis and do away with fantastic methods. Giolitti established definitely the fact that carburization in charcoal is carried on essentially through the medium of carbon monoxide gas and only to a negligible degree by direct absorption of carbon from the charcoal. Later studies have made good use of this knowledge to improve and better control carburizing practice.

Chemistry of Pack Carburizing

The chemistry of carburization in charcoal is based, simply enough, on two reactions, viz., one between CO and the iron:

$$2CO + 3Fe = Fe_3C + CO_2 \qquad\qquad I[3]$$

and the other to regenerate the CO by the action of CO_2 on charcoal:

$$CO_2 + C = 2CO \qquad\qquad II$$

Both of the reactions are reversible and, therefore, the law of mass action determines the extent to which they proceed.

The Mass-Action Law

This law is stated as follows:

A reversible reaction may be written as a chemical equation. When such a reaction reaches a state of equilibrium the quotient, found by dividing the *product of the active masses* on one side of the equation by the *product of the active masses* on the other side of the equation, equals a constant. This constant applies only to one temperature and pressure. In other words, the quotient so found varies with temperature and pressure.

The term active mass requires definition. In a single-phase solution, it may be evaluated as the mol fraction of a constituent in that phase.[4]

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[2] *The Cementation of Iron and Steel*, by F. Giolitti, translated by Richards and Rouiller, New York, McGraw-Hill, 1915.

[3] If one does not accept the assumption that the carbon in austenite is in the form of Fe_3C, the first reaction may be just as well written:
$$2CO + \text{gamma iron} = \text{austenite} + CO_2$$
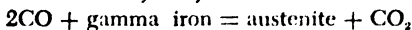
[4] By mol fraction of a constituent is meant the proportion the number of molecules of that constituent bears to the total number of molecules in the same phase. Where compositions are in weight per cent, mol fractions are calculated as follows: (1) Divide the weight per cent of each constituent by its molecular weight. (2) Divide each result, so obtained, by the sum of all the results. This gives mol fractions if the division is indicated. If the division is carried out as a decimal, the results may be expressed in *molecular per cent*.

In the case of gaseous mixtures, mol fractions are in the same proportion as per cents by volume. This is in accord with Avogadro's hypothesis.

However, where a solid phase consisting of a pure element or compound is involved in a reaction with a constituent of a liquid or a gaseous phase, the reaction is assumed to be taking place entirely at the surface of the solid. Here the molecular concentration of the material that composes the solid phase is assumed to be 100%, or unity if expressed as a mol fraction.

When the mass-action law is applied to a chemical equation the molecular concentration (mol fraction) of each constituent is indicated by embracing the symbol for that constituent in brackets. Thus equation I gives

$$\frac{[Fe_3C] \times [CO_2]}{[CO]^2 \times [Fe]^3} = k.$$

which reads, "Molecular concentration of Fe_3C times concentration of CO_2, divided by the concentration squared of the CO times the concentration cubed of the Fe equals the constant k."

We can reason from such an equation that there will be a balance in the concentrations of the reacting substances at any temperature. The determination of the constant k is a matter for chemical analysis. Once it is determined for a particular temperature, it holds for all concentration variations at that temperature.

If, for instance, the CO_2 is increased in the gaseous mixture, it is seen that either the Fe_3C concentration must decrease or the CO concentration must increase in order to maintain the constant.

Intensity and Depth of Carburization

The two important considerations in pack carburizing are depth of penetration of the carbon in a given time and intensity of carburization or maximum carbon concentration. The former is entirely dependent upon the rate of diffusion of carbon through the steel. This rate of diffusion increases with temperature, but recent studies by Mehl and others have indicated that, in the percentages encountered in ordinary steels, most alloying elements (Ni, Cr, Mn, etc.) have little or no effect. Hence, deeper cases are more rapidly obtained at higher temperatures.

The intensity of carburization is dependent upon several factors. If, as noted above, the carburizing reaction

$$3Fe + 2CO = CO_2 + Fe_3C$$
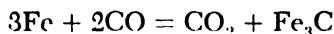
is reversible, it is evident that carburizing should proceed up to some concentration of Fe_3C that represents the equilibrium point in the reaction. This point will depend on the mass action constant, which in turn is different for different temperatures but is not necessarily pro-

portional to temperature. As a matter of fact, with CO gas alone, the highest carbon concentrations are obtained at the lowest temperature at which austenite can exist, viz., the eutectoid temperature.

The equilibrium constant for the regenerative reaction, namely,

$$CO_2 + C \rightleftharpoons 2CO,$$
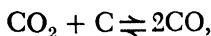
which reduces to

$$\frac{[CO]^2}{[CO_2] \times [C]} = k,$$

also affects the equilibrium. Since C is solid and, therefore, $[C] = 1$, we may write

$$\frac{[CO]^2}{[CO_2]} = k,$$

from which, in a mixture consisting only of CO, CO_2, and C the composition of the gas is dependent on temperature alone.

Special type graphs to describe these effects have been drawn and are very useful in studying carburizing behavior. One such curve by Takahashi (Figure 16.1)[5] shows the equilibrium concentrations of CO in $CO-CO_2$ mixtures in the presence of saturated austenite at various temperatures. This graph is interpreted as follows.
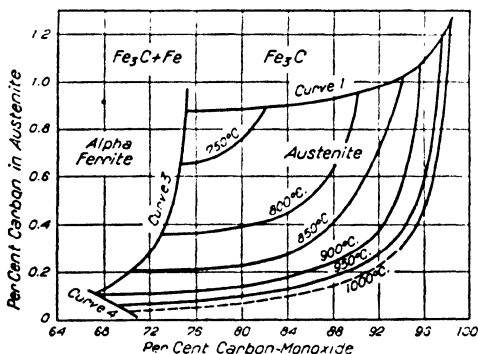
FIGURE 16.1. Equilibrium concentrations of CO and CO_2 with saturated austenite (Takahashi, cited by Grossmann and Webber in *Trans. Am. Soc. Metals, Carburizing Symposium,* 1938).

The isotherms (constant temperature lines) indicate the gas compositions that will neither carburize nor decarburize austenite of various compositions. For instance, at 800°C a gas mixture containing 88% CO and 12% CO_2 would produce no change in a 0.60% carbon steel. However, it would carburize a steel containing less than 0.60% carbon and decarburize a steel containing more than 0.60% carbon. If a higher carbon content than 0.60% were desired in the case at this temperature, a higher CO/CO_2 ratio would be required.

It is perfectly evident from the curves that, for a given gas concen-

[5] "On the Equilibrium between Austenite and the Carbon Oxides," by Genské Takahashi, *Sci. Repts., Tôhoku Imp. Univ.,* 15, 1926.

tration, the lower the temperature the higher will be the carbon content in the case. We thus conclude that in the mass action equation

$$\frac{[Fe_3C] \times [CO_2]}{[Fe]^3 \times [CO]^2} = k,$$

since the numerator is the right side of equation I, k decreases as the temperature increases. This means that higher temperatures tend to reverse the carburizing reaction. At usual carburizing temperatures (1700°F) it is necessary to maintain a CO concentration of 95% or better to reach eutectoid carbon in the case.

Mechanism of Pack Carburizing

We are now able to draw a fairly accurate picture of the mechanism of pack carburizing. Assume the surface of a piece of steel in close proximity to granules of charcoal, and bathed in CO gas (more or less diluted with nitrogen). The temperature is about 1700°F so the steel is in the austenitic condition. CO coming in contact with the steel will decompose according to reaction I, giving its carbon to the austenite and forming [6] CO_2. This CO_2 soon finds its way to a particle of charcoal from which, by reaction II, it is converted to two molecules of CO again.

Energizers

Because of the necessity of maintaining a concentration of CO equal to 95% or better, it is not possible to carburize, in charcoal alone, to much better than eutectoid carbon except at lower temperatures where the penetration becomes very slow. However, when certain inorganic substances, notably barium carbonate, sodium carbonate, or calcium carbonate, are added to the mixture, the intensity of carburization is greatly increased. These substances are called energizers. The most popular is $BaCO_3$. Na_2CO_3 is troublesome because it fuses at carburizing temperatures, and $CaCO_3$ is less effective than the other two. In practice the energizer is intimately mixed with the charcoal. Sometimes the powdered charcoal and energizer are bound together into small pellets with molasses.

The chemistry of the action of energizers is not well understood. Explanations based on the formation of CO_2 by calcination of the carbonates with subsequent conversion of the CO_2 to CO, thus increas-

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[6] Apparently the reversible reaction

$$2CO \rightleftharpoons CO_2 + C$$

maintains a definite concentration of nascent carbon which is the form in which it enters the steel.

ing the CO content of the atmosphere, seem not to be adequate, for it has been noted that the calcined forms, BaO, CaO, Na_2O, when mixed with fresh charcoal are apparently just as effective. The most logical suggestion is that, at the temperature of carburization, the carbonates are *partially* calcined, leaving the oxides as an absorbent for the CO_2 formed by the carburizing reaction and thus keeping it away from the iron. By a sort of three-way equilibrium this might lower the CO_2 concentration below that obtainable with charcoal alone. For instance, the charcoal by reaction II changes the CO_2 to $2CO$. This would unbalance the reaction

$$BaCO_3 \rightleftharpoons BaO + CO_2,$$
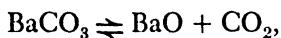
leaving the barium carbonate calcined beyond the equilibrium point. Under these conditions any CO_2 formed by the carburizing reaction would be instantly absorbed by the BaO.

The amount of energizer used in commercial mixtures varies from about 5 to 20% (Bullens-Battelle)[7] although amounts in excess of 2 or 3% are not believed to add appreciably to intensity of carburization.

Intensity versus Depth of Penetration

Although we have adopted the thesis that the depth of penetration is dependent only on diffusion rate for any temperature, yet it must be evident that in the early stages, at least, the concentration gradient will affect this diffusion rate. Especially is this true when methods of measuring depth of penetration are taken into account. Such methods consist usually in estimates based on changes in appearance of the fracture or in microscopic appearance of the section as etched in nitric acid. Naturally the minimum amount of composition change required to show a visible change will be a finite number, usually several tenths of 1% of carbon. The time required to produce such a change at any stated depth from the surface will certainly depend on the carbon gradient.

Conversely, the rate of diffusion will help determine how long it will take, after carburizing starts, for the surface concentration to reach equilibrium with the carburizing mixture. Since diffusion rate is greater at higher temperatures and intensity of carburization can be controlled by varying the carburizing mixture, a considerable variation is possible in the type of case in the finished product. Graphs to show carbon concentration at various depths below the surface are useful

[7] *Steel and Its Heat Treatment*, by D. K. Bullens, revised by the Metallurgical Staff of Battelle Memorial Institute, fourth edition, John Wiley and Sons.

in understanding the progress of carburization. One such (quoted by McQuaid) is reproduced as Figure 16.2.[8]

Except in curves 1 and 2, which were made at low carburizing temperatures, such curves as 3, 4, 5, and 6 will be expected to level off after penetration has progressed beyond a certain point, for instance Figure 16.3.[9]
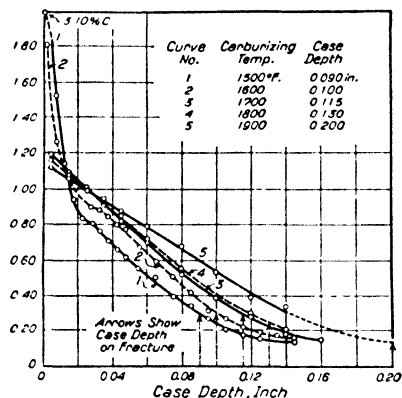
FIGURE 16.2. Carbon gradients in the case; carburizing temperatures as shown (Schlumpf, quoted by Mc-Quaid and in turn by Grossmann in *Trans. Am. Soc. Metals, Carburizing Symposium,* 1938).
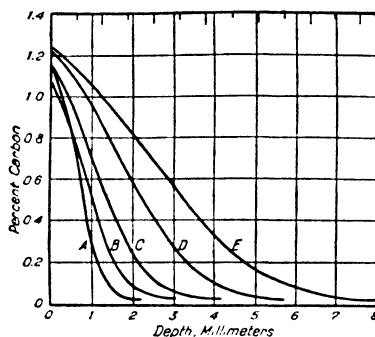
FIGURE 16.3. Depth of carbon penetration versus surface concentration in gas carburizing (Bramley and Lawton, *J. Iron Steel Inst. (British) Carnegie Scholarship Memoirs 1927;* cited by Grossmann in *Trans. Am. Soc. Metals, Carburizing Symposium,* 1938).

The type of case usually desired is one in which there is a gradual increase from the carbon of the core to the maximum concentration at the surface. If the change in carbon content is too abrupt at any zone it causes cracking in subsequent heat treatment.

Gas Carburizing

Although the results of pack carburizing are in general very satisfactory as regards type of case and uniformity of the product, yet the process is mussy and tedious. To quench the pieces from the carburizing temperature is usually impractical so that an extra heating is necessary for heat treatment. This is somewhat objectionable as it may involve a partial decarburization or scaling of the carburized surface if not carried out under ideal conditions of furnace atmosphere. Warping also is increased each time the pieces are heated.

[8] "Fundamentals of Carburizing," by M. A. Grossmann, *Trans. Am. Soc. Metals, Carburizing Symposium,* 26, June, 1938.

[9] "The Gaseous Cementation of Iron and Steel," by A. Bramley and G. Lawton, *Carnegie Scholarship Memoirs, Iron and Steel Institute* (London), 1927.

The advantages to be gained by carburizing in a suitable gaseous atmosphere have long been recognized, but only in recent years have the principles and theory of such processes been sufficiently well understood to bring about their widespread use. Even now there is still much room for research into the behavior of steel with respect to surrounding atmospheres.

Only brief mention will be made here of the special furnace equipment required for gas carburizing. For more extended discussions of this subject the reader is referred to the works already cited—the book by Bullens and the ASM Carburizing Symposium. One type of furnace for small articles is the rotary muffle type in which a rotating cylindrical drum, through which the carburizing gas is passed, slowly tumbles the charge. The drum is heated externally by gas or electricity.

Other types of furnace may be used for heavier articles or pieces that cannot withstand tumbling. Here, uniformity of carburization is obtained by proper circulation of the gas and proper support and stacking of the pieces. Such furnaces may be variously shaped muffles or continuous furnaces in which the charge is carried through on special conveyors.

In spite of the fact that one is not confused by a great array of "patent" mixtures for gas carburizing, the chemistry of the process is even more difficult to understand than that of pack carburizing. True, a number of higher hydrocarbons are used to enrich the carburizing gases, but it can be assumed that these always crack down at the carburizing temperature to *methane* (CH_4) and carbon (soot).

Thus we may assume that the gases with which we have to deal are: CO, CO_2, O_2, H_2O, H_2, CH_4, and the inert gas N_2 which acts only to dilute the other gases. Carbon, in the form of soot, introduces reactions similar to those obtained in pack carburizing.

Since cleanliness is one of the advantages of gas carburizing, the deposition of soot would not be particularly desirable even if it assisted carburization, but it is found that the best carburizing conditions are not, generally, those in which much soot is deposited. In fact, it may seriously hinder carburization. Again, it is a fact that iron oxide scale may form on pieces that are being carburized. This indicates that oxidation-reduction equilibria with respect to the iron are not identical with carburization-decarburization equilibria.

Chemistry of Gas Carburizing

The specific effects of the above gases can be stated only with reservations, since they are greatly affected by temperature and the composition of the mixture. However, we may list their usual behavior:

CO, mildly carburizing; more intense at low temperatures than high.

CO_2, decarburizing, especially at higher temperatures; oxidizing if concentration is greater than that of CO.

O_2, oxidizing but *not* decarburizing in moderate amounts.

H_2O, decarburizing and oxidizing except in very low concentration; a slight amount seems necessary to catalyze the carburizing reactions.

H_2, strongly decarburizing and reducing; with a critical amount of water vapor (10 milligrams per cubic foot of H_2) the H_2 is not decarburizing (Austin).[10]

CH_4, strongly carburizing, somewhat soot forming.

The chemical reactions by which these gases affect the steel and each other are as follows.

Decomposition reactions:

(1) $2CO \rightleftharpoons CO_2 + C$
(2) $CH_4 \rightleftharpoons 2H_2 + C$
(3) $CO_2 + H_2 \rightleftharpoons CO + H_2O$
(4) $CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$
(5) $CO + H_2 \rightleftharpoons C + H_2O$

Carburizing-decarburizing reactions:

(6) $2CO + 3Fe \rightleftharpoons Fe_3C + CO_2$
(7) $2H_2O + Fe_3C \rightleftharpoons CH_4 + 2FeO + Fe$
(8) $2H_2 + Fe_3C \rightleftharpoons CH_4 + 3Fe$

Oxidizing-reducing reactions:

(9) $2Fe + O_2 \rightleftharpoons 2FeO$
(10) $Fe + CO_2 \rightleftharpoons FeO + CO$
(11) $Fe + H_2O \rightleftharpoons FeO + H_2$

All the above reactions are considered to be reversible as indicated by the arrows. However, this is true in some cases only when the gases are impure or when the reaction is catalyzed by the presence of iron or carbon.

The last statement applies particularly to CO, hydrogen, and water vapor. CO does not deposit carbon by itself when heated but gives carbon to iron quite readily by reaction (6). Hydrogen, when very dry, decarburizes slightly. With 10 milligrams of water vapor per cubic foot of H_2 there will be no decarburization, but when increased amounts of water vapor are present the decarburization by hydrogen becomes intense. Pure saturated steam, on the other hand, is only slightly de-

[10] C. A. Austin, *Trans. Am. Soc Metals*, **22**, January, 1934, quoted in article by John A. Webber, *Trans. Am. Soc. Metals, Carburizing Symposium*, **26**, June, 1938.

carburizing, but, as with hydrogen, water vapor seems to exert its greatest decarburizing effects in the presence of other gases.

While hydrogen will, by reaction (11), reduce iron oxide and keep a clean surface on steel, as is done in bright annealing of strip and sheets, it cannot be used for this purpose in the carburizing process because of the decarburizing effect shown in reaction (8).

Equilibria in Furnace Atmospheres

Probably the clearest correlation and understanding of the rather confusing accumulation of data regarding gaseous atmospheres can be obtained by a study of Stansel's curves, shown in Figure 16.4.[11]

In these curves the abscissas represent ratios of the gases indicated. It is assumed that any point on a curve represents the ratio and the temperature of the two gases in a mixture that is neutral toward the steel as regards either oxidation-reduction or carburization-decarburization. The steel is saturated with carbon, that is, it contains the carbon content that is in equilibrium with cementite at the temperature in question. One sees from this curve that at 1600°F a CO_2/CO ratio of .48 would keep iron from scaling but would be badly decarburizing, since to carburize at this temperature the ratio would have to drop below 5%.

FIGURE 16.4. Equilibrium curves for various gases with saturated austenite (Reproduced by permission from *Industrial Electric Heating*, by N. R. Stansel, published by John Wiley and Sons, Inc., 1933; cited by Webber in *Trans. Am. Soc. Metals, Carburizing Symposium*, 1938).

According to the CO_2/CO curves a mixture can be found that at low temperatures will carburize and at the same time oxidize the surface. We cannot expect CH_4/H_2 mixtures to oxidize, but they may carburize or decarburize. The decarburizing effect of hydrogen in curve *B* can be compared to the reducing effect in curve *A*. In the area between these two curves we should find ratios of methane, hydrogen, and water vapor that will carburize and at the same time prevent scaling.

Another point brought out by the curves, both of Takahashi (Figure 16.1) and Stansel (Figure 16.4), is that CO carburizes less in-

[11] *Industrial Electric Heating*, by N. R. Stansel, first edition, 1933, page 226, John Wiley and Sons.

tensely as the temperature rises and a higher concentration of CO relative to CO_2 is required as the temperature rises, if carburization is to continue. On the other hand, methane exhibits the opposite effect and carburizes even when it bears a low ratio to the hydrogen present if the temperature is high (1500°F or better).

One must be careful in reasoning from these observations because of the complexity of the situations in actual practice. For instance, while CO carburizes more intensely at lower temperatures by reaction (6) yet, in the presence of wood charcoal, reaction (2) increases in intensity to the left (that is, $CO_2 + C \rightleftharpoons 2CO$), as the temperature rises, thereby increasing the concentration of CO in pack carburizing at higher temperatures. *The net effect is increased intensity at higher temperatures, in pack carburizing, except as the concentration of carbon at the surface is reduced by more rapid diffusion inward.*

In gas carburizing, on the other hand, CO is definitely less effective and even decarburizing at higher temperatures, since the formation of CO_2 by reaction (6) reverses the reaction. Intense carburization is obtained by the use of methane, natural gas, and higher hydrocarbons, such as propane and butane.

Note: In Chapters I through XIV the questions have been listed in two categories. The questions to follow will not be so divided and, in fact, most of them should be considered as requiring additional information or reading beyond that given in the text.

PROBLEMS AND QUESTIONS

1. Redraw the iron-carbon equilibrium diagram (Figure 9.1) to an atomic per cent basis. Calculate atomic percentages of carbon as described in footnote 4, page 178.

2. Should it be possible to produce crystals of cementite by carburizing at a constant temperature?

3. Describe a mechanism whereby crystals of cementite may form in the carburizing process.

4. If the 900°C isotherm in Takahashi's diagram (Figure 16.1) gives a value of 94.2% CO in equilibrium with austenite containing 0.60% carbon, calculate the equilibrium constant k for the mass-action equation on page 179. *Note:* Count gas percentages as molecular since they are by volume, and count the reactivity of Fe_3C and Fe as proportional to the mol fractions of each in the austenite. [*Ans.* $k = 0.00213$.]

5. Calculate k, using the same isotherm at 88% CO and 0.26% C in the austenite. [*Ans.* $k = 0.00200$.] What unproven assumption might account for the variation in the value for k?

6. Using the value 0.002 for k at 900°C, calculate the per cent CO necessary to carburize to 0.80% carbon. How does this agree with the curve?

7. How does case depth affect the carbon gradient?

8. Replot curve D_1 of Stansel's curves (Figure 16.3) to show the equilibrium for the ratios of CO/CO_2 instead of CO_2/CO.

9. How does the carburizing power of CO compare to that of methane and how does its reducing power compare to that of hydrogen?

10. Suggest a gas composition in which it should be possible to anneal a 0.40% carbon steel at 1450°F without carburization, decarburization, or oxidation of the surface.

CHAPTER XVII

Heat Treatment of Carburized Steel—Liquid-Bath Carburizing

Mechanical Requirements in the Case · Mechanical Requirements in the Core · The Complexity of the Problem · Refinement of the Core and Case · Tempering · Modified Treatments · Liquid-Bath Carburizing and the Cyanide Processes · The Mortal Hazard of Cyanide · The Methods Used · Chemistry of the Cyanide Process · Activated Baths · The Results Obtained in Cyaniding · Optimum Bath Concentrations · The Character of the Case

Having produced by appropriate methods a high-carbon case on a steel article, our next concern is the type of heat treatment that can be used to give both case and core suitable physical properties. This involves, of course, an understanding of what constitutes suitable physical properties in case and core. This point will be considered first.

Mechanical Requirements in the Case

Obviously the case will require the same hardness and resistance to wear that would be expected of a high-carbon steel used in similar service. In some instances, such as bearing parts, balls and sockets, and sliding parts subject to a fairly uniform load, hardness is paramount. In other cases, such as gears and camshafts, where the part is subjected to considerable shock or high local pressures, a certain amount of toughness is desirable. Where both hardness and shock resistance are necessary, as in ball- and roller-bearing parts, the problem is complicated, and alloy steels are frequently employed which can be given great hardness in the carburized zone and yet retain a small degree of ductility.

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Mechanical Requirements in the Core

The requirements for the core are not so easily defined. Except with very thin cases, any ductility the core might have in plastic deformation could not be utilized without destroying the case. On the other hand, a lack of ductility in the core, particularly if accompanied by a non-uniform response to strain, might easily start fractures in the case. In general, the most desirable characteristic in the core is fine grain. If plain carbon steels are used, this fine grain can be secured only by heat treatment since satisfactory carburizing steels are, in general, coarse grained if heated to carburizing temperatures (see McQuaid-Ehn test). With certain alloy steels, on the other hand, the grain structure will be fine even at the carburizing temperature.

With the above considerations in mind, we can outline several types of heat treatment for carburized steels.

The Complexity of the Problem

We must keep in mind that in a carburized piece we have two types of steel to deal with, or possibly three. (See Figure 17.1.)

Consider a core of 0.20% carbon and a case which may reach 1.20% carbon. If properly carburized there will be a considerable zone of 0.80% (eutectoid) carbon a little below the surface. Obviously, if the piece is cooled in the carburizing box from 1700°F (970°C), there will be considerable cementite network in the outer part of the case which will follow austenite grain boundaries. In general, these will be coarse for carbon steels at the carburizing temperature so that the cementite network will be coarse and, consequently, will have an embrittling effect on the steel. The pro-eutectoid precipitation of *both* cementite and ferrite sometimes produces a sharply outlined pearlite zone. According to Giolitti the outer layers of metal may crack away from this zone in subsequent heat treatment, a defect known as *exfoliation.*

The core of such a piece of steel will have been heated only a little above its Ac_3 point and, except for the long sojourn at the carburizing temperature, should have a fairly fine ferrite grain structure. However, this is amenable to some improvement.

The pearlite zone has been heated far above its critical temperature and has descended from coarse austenite grains.

The most objectionable of all these conditions is the coarse cementite network in the outer case. This will require a high reheating temperature for a long time prior to quenching to be completely re-dissolved

in the austenite. This in itself is a strong argument for gas carburizing wherein the piece can be quenched from the carburizing temperature and the cementite prevented from separating as a network. Attempts have been made to water-quench pack-carburized pieces by throwing them first on a screen to remove the carburizer. Such methods have their limitations, however. Probably a better method is to control the carburizing mixture so as to avoid a hypereutectoid case, but this cannot be done if the higher carbon is required.

Refinement of the Core and Case

At any rate, if core refining treatment is needed, the piece will be heated a little above Ac_3 for the core, and quenched in water or oil. This will give a minimum grain size to the ferrite of the core and will distribute the carbon of the core so as to increase its strength. If the core is low in carbon it will still be ductile. The case will now be in a hardened condition but coarse grained, even if the cementite is all in solution. If this treatment is now followed by a reheating to just above Ac_1 and a quenching (called a "regenerative quench"), a fine grained case will result. If the grain boundary cementite had been all in

FIGURE 17.1. Relation of carbon concentration to the critical range.

solution before this last treatment the effect will be to spheroidize all cementite in excess of that represented by the A_{cm} line at the temperature reached (see Figure 17.1). This spheroidized cementite does not have the embrittling effect of the grain boundary cementite and, being quite finely divided, increases the hardness. The core is now in what might be called a fully tempered condition. Its grain size has not been materially altered.

Tempering

The final treatment will consist of a tempering operation to toughen the case. The extent of this will depend on the hardness desired.

Other treatments applied to the case carburizing process consist of annealing or normalizing prior to carburizing for the purpose of reducing warpage and improving machinability.

To recapitulate, the complete heat treatment involved in the pack carburizing process is outlined as follows:

A. Preliminary treatment before carburizing:
    1. Normalize or anneal to minimize warpage.
    2. Machine.
B. Carburizing:
    1. Carburize at 1700° to 1750°F.
    2. Cool in air or in the carburizing box.
C. After carburizing:
    1. Reheat to 1650° to 1700°F and quench in oil. This treatment refines the grain of the core and dissolves the carbides of the outer case.
    2. Reheat to 1350° to 1400°F and quench in water or oil. This hardens case, tempers the core, and spheroidizes the carbides (regenerative quench).
    3. Temper to proper case hardness.

Modified Treatments

Only rarely is this full treatment used in practice. Treatment C–1 is frequently omitted or else substituted for C–2. Pieces are sometimes separated from the carburizing mixture while hot and quenched directly with no other treatment but tempering. Such procedure is not recommended, however, for important work. With alloy steels that do not develop coarse grain at the carburizing temperature, it is usually advisable to eliminate at least one of the quenching operations.

With gas carburizing where the pieces can be quenched in oil or water from the carburizing temperature, considerable modification of the above program is possible and usually advisable. It must be remembered that warpage is increased each time the piece is heated. Furthermore, it is generally conceded that frequent reheatings are not beneficial to steel quality. They increase tendencies to cracking on quenching and seem to promote general unreliability.

A schematic diagram to show the various treatments that are applied commercially to carburized steel has been published by the International Nickel Company and is also printed in the *National Metals Handbook*. It is reproduced in Figure 17.2.[1]

In the diagram the lines sloping downward indicate slow cooling from the carburizing temperature. Vertical lines indicate quenching or heating. Treatments A, B, and C *may* be used on coarse-grained steels, but, obviously, refinement of case and core is a compromise.

[1] "Case Hardening of Nickel Alloy Steels," *Nickel Alloy Steels*, 1934, Sec. 6, No. 5, International Nickel Company; quoted by National Metals Handbook.
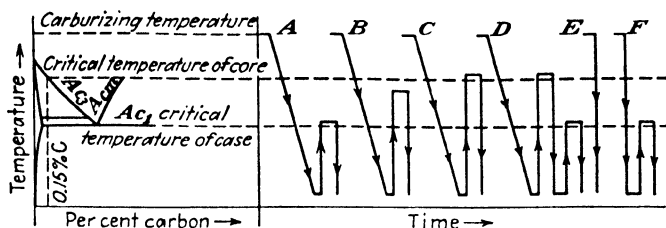
Treatment	Case	Core
A. Best adapted to fine-grained steels	Refined; excess carbide not dissolved	Unrefined; soft and machinable
B. Best adapted to fine-grained steels	Slightly coarsened; some solution of excess carbide	Partially refined; stronger and tougher than (A)
C. Best adapted to fine-grained steels	Somewhat coarsened; solution of excess carbide favored. Austenite retention promoted in highly alloyed steels	Refined; maximum core strength and hardness. Better combination of strength and ductility than (B)
D. Best treatment for coarse-grained steels	Refined; solution of excess carbide favored; austenite retention minimized	Refined; soft and machinable; maximum toughness and resistance to impact
E. Adapted to fine-grained steels only	Unrefined with excess carbide dissolved; austenite retained; distortion minimized; file proof when carbon is high	Unrefined but hardened
F. Adapted to fine-grained steels only	Refined; solution of excess carbide favored; austenite retention minimized	Unrefined; fair toughness

FIGURE 17.2.   Heat treatments applied to carburized steel.

The double quench of treatment D refines both case and core. Treatments E and F quench directly from the carburizing treatment.

Liquid-Bath Carburizing and the Cyanide Processes

Heat treatment in baths of molten salts is a very interesting subject from the standpoint of the steel treater and is of considerable commercial importance. This is particularly true of the case-carburizing processes that depend on immersion of the steel in molten alkali cyanides and calcium cyanide. However, from the standpoint of metallographic structures it is of secondary importance and will be treated but briefly.

All carburizing processes in liquid baths depend upon the reactions by which sodium cyanide NaCN, potassium cyanide KCN, and calcium cyanide $Ca(CN)_2$ give carbon and nitrogen to the steel surface. That nitrogen is partly responsible for the intense hardness of cyanide cases was long ago suspected but has been definitely ascertained in recent years.

The Mortal Hazard of Cyanide

Attention must be called to the fact that cyanides are fatally poisonous if taken internally, even in minute quantities. They are dangerous even on the skin, particularly in cuts. One should never attempt to use them as antiseptics. Hydrogen cyanide HCN, produced by the action of acids on cyanides, is extremely poisonous to breathe. However, not to give a false impression, it should be pointed out that the fumes which are seen escaping from cyanide pots where cyaniding of steel is done are not cyanide but rather carbonates formed by the decomposition of cyanide at the high temperature. It has been found that, with reasonable precaution to avoid or remove these fumes, accidents in cyaniding plants are practically non-existent.

The Methods Used

The cyaniding processes might be divided into three categories. The first process is the oldtime blacksmith's method of heating the steel above Ac_3, dipping it into or sprinkling it with potassium or sodium cyanide powder, continuing the heating until the powder is entirely melted and coats the piece, and then quenching. This gives a very hard, very superficial case. The second is the usual process of producing a thin, superficial case, by immersion for from five minutes to an hour in a molten mixture of sodium chloride, sodium carbonate, and sodium cyanide. Other salts, such as $BaCl_2$, $CaCl_2$, borax, or B_2O_3 may also be used. The third type of process differs from the second only in the introduction of calcium cyanide into the molten bath. This is called an "activated" bath. However, the use of the calcium cyanide involves a somewhat different reaction from that obtained with sodium or potassium cyanide.

Chemistry of the Cyanide Process

There seem to be two reactions with sodium cyanide. The first is:

$$2NaCN + 2O_2 = Na_2CO_3 + CO + 2N. \qquad (1)$$

This reaction liberates nascent nitrogen and CO.

The second [2] is:

$$6NaCN + 3O_2 = 2NaCN + 2Na_2CO_3 + 2C + 4N. \qquad (2)$$
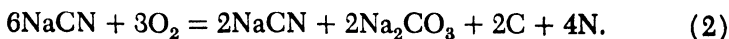
This reaction liberates nascent carbon and nitrogen.

It is noted that both these reactions require oxygen and it has been observed that if the bath is kept out of contact with air the action is slowed down.[3]

The effect of the nitrogen liberated in these reactions is important. Iron absorbs nitrogen (presented in nascent form) at temperatures above 900°F (482°C) and under non-oxidizing conditions. The nitrogen forms extremely hard intermetallic compounds with the iron, namely, Fe_6N, Fe_4N, and Fe_2N; besides, it is slightly soluble in the ferrite and quite soluble in the austenite.[4]

For deep penetration of nitrides, special steels are treated with dry ammonia gas as in the nitriding process, but in cyaniding, the penetration of nitrogen is only a few thousandths of an inch. This gives a very great surface hardness to cyanided steels; harder than could be obtained with carbon alone. However, the rate of diffusion of nitrogen is lower than that of carbon so that the interior of the case is usually higher in carbide while the exterior is higher in nitride. Longer times in the cyaniding bath promote an increased thickness of the carbide case with less increase of the nitride case.

Likewise, the promotion of a deeper carbide case is favored by higher temperatures, whereas the nitride case is more rapidly deepened at temperatures within the critical range.

Activated Baths

To explain the behavior of activated baths, the reaction may be written

$$Ca(CN)_2 = CaCN_2 + C.$$
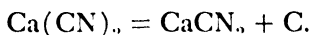
The carbon in nascent form is a strong carburizer and increases the carburizing tendency of such baths at the expense of the nitriding tendency.

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[2] Combining the two reactions:
$$2NaCN + O_2 = 2NaCNO,$$
$$3NaCNO = NaCN + Na_2CO_3 + C + 2N.$$
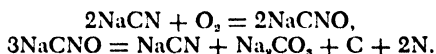
[3] *Steel and Its Heat Treatment*, by D. K. Bullens, revised by Metallurgical Staff of the Battelle Memorial Institute, fourth edition, John Wiley and Sons, I, page 346.

[4] "The Iron Nitrogen System," by Samuel Epstein, *Trans. Am. Soc. Steel Treating*, 16, 5, October, 1929.

The Results Obtained in Cyaniding

The following data taken from the *National Metals Handbook* will give some idea of the actual results to be expected from the cyaniding process.

1. An SAE 1020 steel held for one hour in a bath at 1550°F developed a case depth of 0.010 inch with a maximum carbon content of 0.62%. Held for three hours, the same steel had a case depth of 0.018 inch. The maximum carbon content was 0.74%.

2. The effect of temperature is indicated by a steel that showed a case depth of 0.0005 inch when held in a bath at 1300°F for thirty minutes. The same length of time at 1600°F gave a case depth of 0.0048 inch. In other words, penetration was about ten times as fast at 1600° as at 1300°F.

3. The effect of cyanide concentration in the bath is noteworthy. In thirty minutes at 1500°F the following results were obtained:

NaCN	Case Depth
5.2%	0.002 inch
10.8%	0.004 inch
15.1%	0.005 inch
20.8%	0.0055 inch
30.2%	0.006 inch

Above 30% no increase was noted up to and including 94.3%.

Optimum Bath Concentrations

Since much cyanide is lost by decomposition in high concentration baths, it is important from an economy standpoint to keep the bath as near 30% as possible. This is generally agreed upon as the optimum concentration.

The Character of the Case

It is noteworthy that the carbon is not high in cyanided steels so that the extreme hardness of the case must be attributed to nitride. As shown in Figure 17.3, this nitride is frequently observable in the microsection of slowly cooled pieces as short, straight, dark needles scattered quite uniformly about; the same as are frequently observed in electric welds. When much carbide (pearlite or troostite) is present, however, the identity of the needles is lost, and in rapidly cooled or heat-treated pieces the nitride forms finely dispersed structures just as does the carbide.

FIGURE 17.3. Nitride needles in ferrite, 200×.

QUESTIONS

1. If a carburized round bar of low-carbon core and hypereutectoid case is quenched rapidly from the carburizing temperature, what should be the first portion to transform and why?

2. Which should produce the greater internal stress, the first portion to transform or the last?

3. Describe the structural changes that take place in a hypereutectoid case when it is reheated to just above Ac_1, after having been quenched from above Ac_{cm}.

4. What is a regenerative quench? What is its purpose?

5. Why should steel warp when heat treated?

6. What carburizing process or processes would you select for each of the following problems and why? (a) camshafts for automobile engines where high wear resistance is required in the cams and toughness in other parts; (b) races for ball or roller bearings—these require hard surfaces that will not crack, plus over-all strength; (c) armor plate, requiring resistance to penetration and cracking; (d) a special attachment you have designed to hold the trailer to your automobile—it is of intricate shape with machined surfaces, but must be very strong; (e) key levers for typewriters and adding machines. They are punched out of sheet and later hardened.

7. In what way should sodium cyanate (NaCNO) be beneficial to a cyanide bath?

8. Is further heat treatment necessary after cyaniding? Why?

CHAPTER XVIII

The McQuaid-Ehn Test: Hardenability

Ailing Steels · A Method of Study and Evaluation · Normal versus Abnormal Steels · Austenitic Grain Size · Factors which Affect Normality and Grain Size · Hardenability · Tests for Hardenability · The Mechanism of Hardening · Hardenability as Related to the S Curve · Summary of Factors in Hardenability

Ailing Steels

It has long been observed that some steels do not respond satisfactorily to hardening treatments. Particularly is this true of steels that have been case carburized. For many years prior to 1922, heat treaters were tormented by the fact that occasional batches of steel would not develop the desired hardness when carburized and quenched, or would exhibit local soft spots on the surface after that treatment. There seemed to be no way of anticipating such conditions and much time and material was wasted because of rejections. The difficulty was attributed to a great variety of causes, and everybody concerned, from the steel manufacturer to the heat treater, came in for criticism.

In 1922 H. W. McQuaid and Eric W. Ehn [1] published the results of their extensive research on carburizing steels for the Timken Roller Bearing Company. There was nothing particularly new or unusual about their procedure, which consisted chiefly of a microscopic study of the carburized zone of the various steels after a standard carburizing treatment. However, their keen observation and careful recording and tabulation of results yielded information which has had profound

[1] "Effect of Quality of Steel on Case Carburizing Results," by H. W. McQuaid and E. W. Ehn, *Trans. Am. Inst. Mining Met. Engrs.*, **67**, 341, 1922.

effects on the manufacture and treatment not only of carburizing steels but also many other steels. As a result of this work, it is possible to distinguish easily the steels that will harden properly from those that develop soft spots and are hardened with difficulty after carburizing.

The theories advanced by McQuaid and Ehn to account for their results are not freely accepted by others, but at least they paved the way for much extended research that has resulted in great advances in our understanding of heat treatment.

A Method of Study and Evaluation

In spite of the name McQuaid-Ehn test, there is no strictly standard procedure that is adhered to by all plants for all steels. Rather, a loosely outlined plan is adapted to work at hand and in such a way as to simulate operating conditions and insure uniformity in the commercial product. Roughly, the procedure is to carburize the pieces to be tested in a suitable standard carburizing mixture for a long enough time to insure a hypereutectoid zone in the case, and then cool slowly enough to form an annealed-type structure. The carburizing temperature is usually around 1700°F, and cooling may take place in the carburizing box. The carburizer may be a commercial mixture or a barium carbonate-wood charcoal mixture containing from 5% to 20% barium carbonate. The carburizing time for carbon steels will be from eight to twenty hours.

Two observations are made on microsections of the pieces thus carburized. First, a study of the pearlite and cementite of the carburized zone classifies the steel as to normality or abnormality. Second, a grain-size classification is made of the hypereutectoid zone.

As first observed, the normal steels hardened properly and the abnormal did not. However, it must not be inferred that this is a criterion of quality in steel. It merely states that abnormal carbon steels do not carburize and harden as they should. For many purposes, the abnormal steels are preferred to normal steels, and steelmakers can now control this characteristic to meet demands.

Normal versus Abnormal Steels

In normal steels the pearlite is completely laminated. This is the outstanding characteristic and the first looked for in determining normality. In the abnormal steels the cementite of the pearlite will appear partly or entirely spheroidized, i.e., it will be like spheroidite, even though the cooling has been from above Ac_3 (or Ac_{cm}). The cementite lamellae appear short or broken. In the normal steels the proeutectoid

cementite network touches the cementite of the pearlite, and usually there are some cementite needles (or plates) within the pearlite grain. In the abnormal steels the network cementite has a margin of clear ferrite on each side, and even in the pearlite grains there may be massive areas that are all ferrite. No cementite needles will appear. Figure 18.1 illustrates normal and abnormal steels.
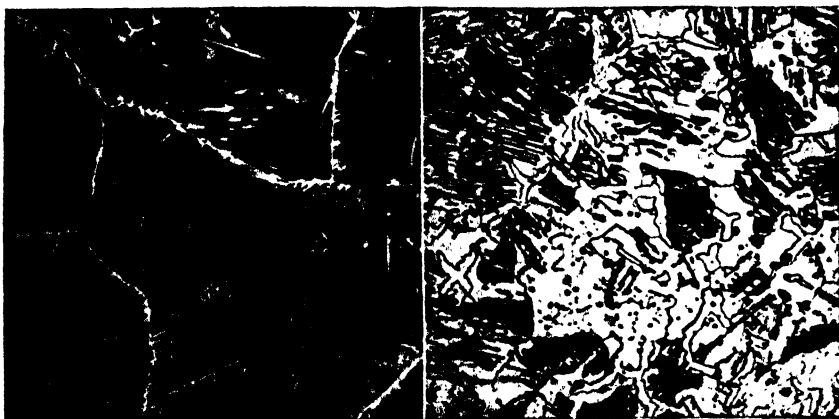
FIGURE 18.1. Left, normal steel; right, abnormal steel; 100×.

Of course, there is no sharp line between these two types of steels and there are intermediate types whose classification will depend upon the person who makes the test and upon the conditions of use to which the steel is put. In some laboratories, several degrees of abnormality are considered, with standard specimens and photomicrographs for each degree. Any test specimen is classified by comparison with these types.

Austenitic Grain Size

The second observation that is made on the carburized specimens is the grain size in the hypereutectoid zone. This may be determined by actual measurement, using an eyepiece micrometer scale or similar device, or by comparison with standard patterns. The latter method is much easier and quicker and just as accurate.

The grain size charts prepared by the American Society for Testing Materials are Standards. These may be found in the 1946 Book of ASTM Standards, Part 1-A, Plates I and II; Designation E-19.

This grain size is, of course, the size of the pearlite patches enclosed by the cementite network. Since we may assume that the cementite network was formed at the austenite grain boundaries as the steel

cooled from the carburizing temperature, the grain size is that of the austenite. It must be emphasized, however, that this austenite grain size is only the size to which the austenite grains had grown at the carburizing temperature (1700°F).

Nevertheless, it was soon found that there is a definite correlation between the austenite grain size of the McQuaid-Ehn test and the degree of normality. Normal steels are coarse grained and abnormal steels are fine grained. Of course, reheating a coarse-grained normal steel to just above Ac_{cm} and cooling quickly will result in somewhat finer grain and will eliminate the cementite grain boundaries. A second heating to just above Ac_1, and quenching, will give a *very fine* grain to the finished product. This is the reason for the elaborate heat treatments recommended for carburized steels in the preceding chapter. However, the problem is often better solved with alloy steels in which good hardenability can be secured in spite of abnormality and fine austenite grain size. This will be discussed in the chapter on alloy steels.

Factors which Affect Normality and Grain Size

There has been much study and research as to the cause of abnormality and a complete explanation is yet to be had. However, it is known to be associated with certain conditions of manufacture of the steel and to be affected by certain variables in composition. It has been observed (by Herty and others) that perfectly pure iron-carbon alloys are neither normal nor abnormal. That is, they show a type of carbide distribution that is different from lamellar pearlite and different from the divorced cementite structure. In the commercial steels, a high oxygen content in the molten steel usually results in abnormality, particularly if the steel is killed with much aluminum. On the other hand, steels in which the manganese content is near the high side of the specification tend to be normal and coarse grained.

The use of aluminum to produce fine-grained carbon steels has become standard practice with steelmakers, and specifications for fine-grained steels usually require a definite aluminum addition in the ladle. Such steels are used for deep drawing sheets and plates that are to be cold pressed into tortuous shapes, such as automobile bodies and fenders. In such steels the fine grain helps to eliminate stretcher strains (strain lines or *Luder's lines*) in the finished articles.

For carburizing steels and steels to be heat-treated, however, the fine-grained abnormal steels simply will not work. Therefore, if carbon steels are used, a coarse-grained normal steel must be selected. The

manufacture of such a steel requires slow finishing in the open hearth to eliminate the oxides as far as possible and then, finally, deoxidizing as far as practicable with manganese and silicon or else resorting to rimming.[2] Little, if any, aluminum is used. As will be noted in a later chapter, alloy steels can be made which will have fine grain and yet show good heat treatment qualities. Vanadium and columbium are the alloys most used for this purpose.

Hardenability

Since steels vary in their behavior on quenching, it is necessary to consider the variations that may occur. First, we may assume that the surface hardness, which can be produced on water quenching, will increase with the carbon content, up to eutectoid carbon, at least.

However, we have seen that the abnormal, fine-grained steels do not harden as well as the normal coarse-grained steels; and further, we find that in medium-sized pieces the hardness is not the same in the interior of the piece after quenching as at its surface (in straight heat-treated steels not carburized). The way in which the hardness of a quenched piece drops off, from outside to center, is a measure of what is termed its hardenability.

Radius, inches
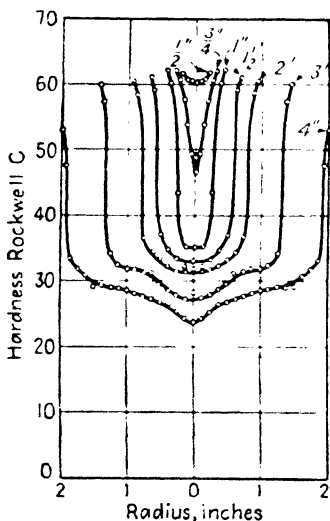
FIGURE 18.2. Hardenability curves for transverse-section method (from "Hardenability of Alloy Steels," by W. E. Jominy, *Trans. Am. Soc. Metals*, 1939, page 75).

Tests for Hardenability

Much work has been put into evolving a method of determining hardenability and the hardening characteristics of steels. For round sections the simplest method is to cut a section across the round and make hardness tests across the face of the section with a Rockwell or Vickers hardness testing machine. The hardness values so obtained are plotted as ordinates on a graph

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[2] Rimmed steel is finished in the open hearth with very little deoxidizer of any kind. After it is poured into an ingot mold it effervesces or "boils" in such a way as to produce a churning action in the mold. Large dendritic growths, which might entrap the gases liberated, are avoided and these gases are eliminated as the metal freezes. The last portion to freeze frequently boils up a little but this is overcome by placing an iron plate or cap on the top of the ingot.

in which the abscissas represent distances from the surface of the specimen.[3] Such curves are shown in Figure 18.2.[4]

As pointed out by Jominy, it is only necessary to plot the curve from outside to center, although the complete traverse is usually shown.

An objection to such curves is that they differ considerably with the size of the test piece so that results on one size cannot be used to predict the curve for another size. Shape also affects the results and the depth of hardening in a plate is not, in general, the same as that shown for a round bar by this test.

The Jominy Test

A method that has become more popular and which overcomes these objections to some extent is the Jominy end quench. The test bar is a 1-inch diameter round, 4 inches long. One end is cut squarely across the piece. The other end is drilled and threaded to accommodate a machine screw or other device by which the piece may be suspended with its axis in a vertical position. The quenching equipment consists of a vertical water pipe, $\frac{1}{2}$ inch in diameter, which supplies a steady fountain of water $2\frac{1}{2}$ inches high. When the specimen is suspended directly over the orifice of this pipe, the squared lower end is drenched with water. No water touches the side of the specimen. A valve is arranged that instantaneously turns the water on full when the specimen is in place.

In operation the specimen is heated to a suitable quenching temperature in a furnace. The heating and holding at temperature follow standard practice. After the proper time has elapsed, the specimen is removed from the furnace and placed in the suspended position above the quenching nozzle. The water is turned on immediately and allowed to impinge on the bottom end of the specimen for about fifteen minutes. At the end of this time the entire specimen is cold enough to touch. A flat place is then ground or machined on the side of the specimen and Rockwell hardness tests are taken every 1/16 inch along its length. The results are plotted in a curve such as that shown in Figure 18.3.

For sections smaller than one inch in diameter, specially designed holders are used that fit around the specimen and present its end to the stream of water. Since the quench is from the lower end up, the metal holder quenches in about the same way as the specimen, and

[3] "Hardenability Tests," Walter E. Jominy, *Metals Progress*, April, 1941, page 447.

[4] "Hardenability Tests," Walter E. Jominy, Hardenability of Alloy Steels Symposium, *American Society for Metals*, October, 1938.
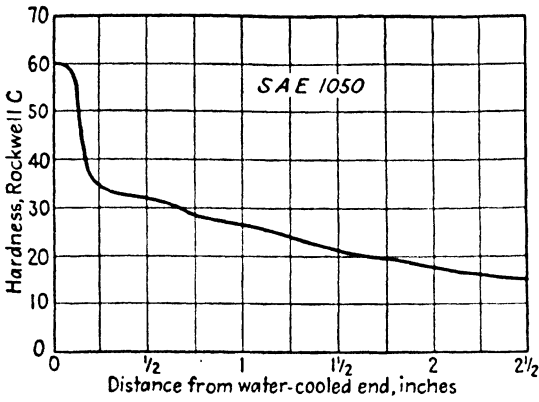
FIGURE 18.3.   Hardenability results of Jominy end quench.
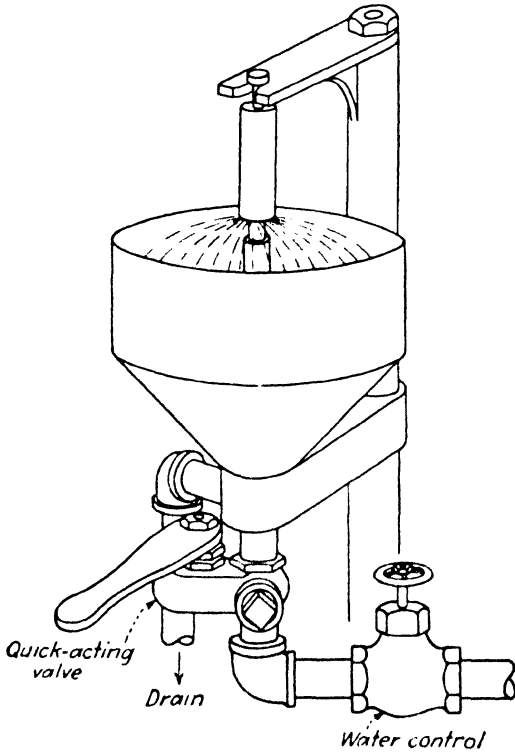
FIGURE 18.4.   Apparatus for Jominy end-quench hardenability test.

the size of the specimen is not so important. Figure 18.4 shows a design of the quenching equipment.

Other Methods of Estimating Hardenability

The depth of the hardened zone may be roughly estimated from the appearance of a fractured bar. The portion that is martensitic shows a finer grain and flatter appearance than the unhardened pearlite portion. Another method is to rough polish and etch a section. The darkest zone under this treatment is that which is bainite. It is just inside the martensitic zone and therefore marks the effective depth of hardening. These two methods, however, do not indicate the quality of the hardened portion (the hardness obtained), nor the actual drop in hardness of the central portion.

The shape of the hardenability curves enables us to correlate much of the information and data that were derived from the McQuaid-Ehn test and the S curve. Hardenability curves show varying degrees of decreasing hardness in passing from the outside to center of a piece of steel. In a normal coarse-grained steel, the hardening will be deep, whereas for an abnormal fine-grained steel the hardening will be shallow (Figure 18.5).
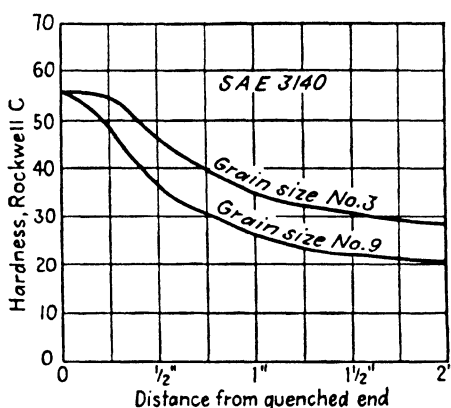
FIGURE 18.5. Hardenability of normal coarse-grained steel and shallow hardening of fine-grained steel.

The Mechanism of Hardening

We may now allow ourselves a little speculation regarding the reasons for these relationships.

In the first place, when a bar of steel is cooled rapidly, heat is transferred from the surface of the piece to surrounding media. Since this takes place very rapidly in water quenching, we can assume that it requires but a few seconds to reduce the surface temperature to a value low enough to promote the formation of martensite.

On the other hand, when we consider the interior of the piece we see that its rate of cooling depends upon the heat conductivity of the metal. This has a value that is independent of the quenching medium

so that there will be a maximum rate of heat removal at any point in the interior of the piece that cannot be exceeded no matter how severe the quench.

Hardenability as Related to the S Curve

Now, if we reconsider the S-curve diagram (Figure 14.9), we will note that there is a temperature in the neighborhood of 550°C at
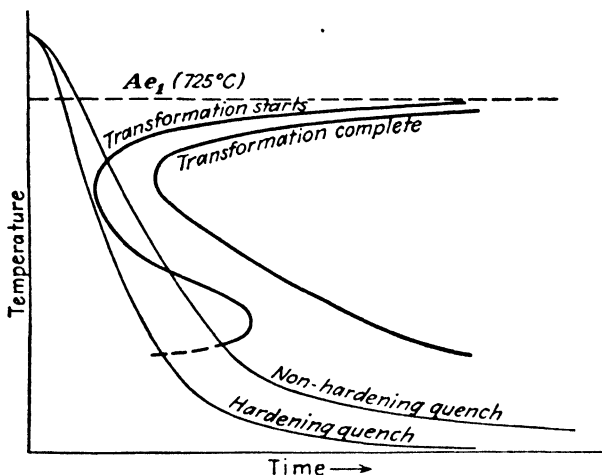
FIGURE 18.6. Cooling curves of hardening and non-hardening quenches in relation to S curve.

which the transformation is most rapid. If a steel is cooled with sufficient rapidity to remain untransformed at that temperature, it will not transform until the change to martensite (200 –300°C) takes place. This is the condition necessary for hardening.

Therefore, in the hardenability curve, the point at which the hardness drops off is the location at which the rate of cooling (by conduction) is less than that required to miss the upper bend in the S curve (Figure 18.6).

For different steels the S curves are different and the farther to the right the S curve lies, the more easily and deeply will the steel harden. This is the same as saying that the lower the transformation rate, the more deeply will the steel harden.

Summary of Factors in Hardenability

Thus, hardenability is apparently related to a tendency to supercool past the temperature of maximum transformation rate. In a carbon steel this tendency is *increased* by the following factors: (1) coarse

grain; (2) homogeneity of the austenite, i.e., no composition gradients; (3) absence of nuclei to start the precipitation of ferrite or carbides; (4) a high temperature prior to quenching—this tends to homogenize the steel as does, also, a long sojourn above A_3; in addition it has a tendency to increase grain size.

The supercooling tendency is *reduced* by the following factors: (1) fine grain; (2) composition gradients in the austenite; (3) anything that may act as nuclei for the start of precipitation of ferrite or carbides—such precipitation usually starts at austenite grain boundaries and therefore fine-grained austenite does not supercool or harden as readily as coarse-grained austenite; (4) dispersed material that may act as nuclei for precipitation; for example, aluminum oxide, present in killed steels, is such a material.

Thus, in reality, the abnormal steels by the McQuaid-Ehn test might be considered to behave in a more normal manner than those called normal inasmuch as the former return more rapidly to equilibrium.

QUESTIONS

1. What is the outstanding characteristic of steel that is rated as abnormal by the McQuaid-Ehn test?

2. Have eutectic or eutectoid structures any single characteristic that distinguishes them from other types of aggregate? If so, describe it. Does abnormal steel exhibit this characteristic?

3. Is the ferrite grain size related in any way to the austenite grain size? If so, what is the relationship?

4. How would you expect the austenite grain size to affect the S curve for a steel?

5. Is a steel that exhibits a coarse network necessarily normal? And is a steel that exhibits a fine network necessarily abnormal? Why?

6. Should it be possible, by heat treatment, to produce in a normal steel a structure resembling abnormal steel?

7. Does the work of Sims and Dahle on the effect of aluminum, discussed in Chapter XII, suggest a possible explanation of the effect of aluminum on grain size?

8. Should the temperature from which a steel is quenched have any effect upon its ability to harden? Explain.

9. What is the minimum cooling rate obtainable in the Jominy end-quench test?

10. Why is it not quite correct to assume (as in Figure 18.6) that the rate of cooling for which the time temperature curve is just tangent to the nose of the S curve marks the dividing line between a hardening and a non-hardening quench?

The Alloy Steels and Other Alloys of Iron

The Most Effective Alloying Element

The effect of carbon in modifying the properties and character of iron is unique. In no other known case can such small amounts of a substance produce such an array of useful characteristics in a metal. Many of the metals that form alloys with iron are themselves more nearly like iron than are some of the iron-carbon alloys. This is true of nickel, cobalt, and chromium. The reasons for this remarkable effect are fairly well understood as a result of chemical, microscopic, and x-ray studies. The low atomic weight of the element carbon, the structural nature of the carbide of iron, and the allotropic transformations that take place in iron are the factors that enter into the explanation of the behavior of the iron-carbon alloys.

For this reason we were eminently justified in spending a great deal of time in the study of the iron-carbon relationships rather than those

of some other iron alloy. The alloy steels are in reality iron-carbon alloys, the properties of which have been modified by the addition of a third element. The addition of such elements to *pure iron* has relatively small effect and limited importance industrially. It is essential, therefore, that we keep in mind the iron-carbon relationships while studying the alloy steels. ·

Composition Ranges in Alloy Steels

Although a number of alloys of iron and carbon which are important industrially contain another element in quite large amount, the majority of the so-called alloy steels contain less than 5% of the third element. Notable exceptions are stainless steel containing from 12 to 20% chromium, Hadfield's austenitic manganese steel containing 12% manganese, and high-speed steel containing about 18% tungsten. The majority of automotive steels, forging steels, case carburizing steels, and much of the sheet and strip steels in which alloys are added contain less than 5% of any element other than iron.

Definition of Alloy Steels

A definition of alloy steels would describe them as steels consisting of iron, carbon, and greater percentages of other elements than are usually found in carbon steels, the extra elements having been added for the purpose of modifying the properties of the steels and making them different from those of carbon steels. As a matter of fact, any single characteristic may be obtained as well in carbon steels as in alloy steels, but certain combinations of properties are possible in the alloy steels that are not possible in the carbon steels. For example, no steel will be harder than the hardest carbon steel, nor will any steel be more ductile than pure iron, but with certain alloys a steel can be produced that gives a combination of hardness and ductility that is not obtainable in carbon steels.

The elements that are added to make alloy steels are referred to as *special elements,* or simply *alloys.* For instance, if we speak of nickel steel, we may say that nickel is the special element, or that nickel is the alloy. Alloy steels are sometimes called special steels, probably for no very carefully considered reason.

Method of Study of Alloy Steels

At first thought it might be suspected that the study and classification of alloy steels would be enormously complicated. Each element has its own equilibrium relationships with iron as well as with carbon, and these relationships (perhaps intricate) will be affected by all the

complicated iron-carbon relationships. To make such a study by equilibrium methods would require a multiple-component diagram. A three-component diagram is the limit of geometrical construction,[1] and, therefore, for more than this number such a diagram would be a practical impossibility. Fortunately, the fact that most alloy steels contain relatively small amounts of the special elements makes it possible to approach the classification of their effects from another standpoint, that is, simply, to determine the specific effect of a small amount of the special element on the iron-carbon relationships and to assume that more of the element will increase the effect. This works all right, within the limits stated, for most elements. The number of possible effects is quite limited, and they can be stated simply.

Effects of Special Elements on Iron-Carbon Relationships

Carbide-Forming and Non-Carbide-Forming Elements

First, we may divide all elements into two classes, carbide-forming and non-carbide-forming. Those that form carbides will naturally be expected to rob some of the iron of its carbon and to introduce the effects of their own carbides in place of Fe_3C.

Elements that form carbides are:

Elements		*Carbides*	*Remarks*
Manganese	$\rightarrow$	Mn_3C	This forms solid solutions with Fe_3C.
Chromium	$\rightarrow$	Cr_4C or Cr_2C	Carbides form solid solutions with Fe_3C.
Tungsten [2]	$\rightarrow$	WC	W, V, and Mo may form double carbides
Vanadium	$\rightarrow$	V_4C_3	with the iron, but when present in suf-
Molybdenum [2]	$\rightarrow$	Mo_2C	ficient amounts may take all the carbon from the iron.
Titanium			Ti and Cb form very stable carbides in-
Columbium			soluble in gamma or alpha iron.

Elements that do not form carbides in steel are copper, nickel, cobalt, silicon, aluminum, and zirconium.

[1] Three-component diagrams have been constructed for a number of metallic systems including some of the iron alloys. This involves a triangular base, and liquidus and solidus surfaces on three-dimensioned equilibrium regions. To be correct, the diagram must be constructed as a plaster or wood model in which the parts fit together like puzzle blocks. Because of the complexity of such a diagram, its purpose, namely, to simplify the tabulation of data, is largely defeated. Many simplifying devices have been devised, however, such as two-dimensional sections through such a diagram, and contour lines to indicate irregular surfaces. Much practice is necessary to be able to interpret such diagrams and patterns.

[2] The actual carbides formed with tungsten or molybdenum are more complicated than the formulas shown here and depend upon the amount of carbon and alloy present. These formulas apply with minimum concentrations of the alloy. Carbides of lower carbon ratio appear at higher alloy concentrations.

Compatibility of Crystal Structure

Second, we may classify the elements according to whether they have a face-centered, body-centered, or other crystal space lattice. In this classification we may expect the face-centered cubic elements to form solid solutions with the austenite, or gamma iron, whereas body-centered cubic elements should form solid solutions more readily in the alpha iron, or ferrite.

Face-centered cubic elements are: aluminum, copper, nickel, cobalt. Body-centered cubic elements are: chromium, molybdenum, tungsten, vanadium. Hexagonal close-packed (closely related to face-centered cubic) are: cobalt, titanium.

Other systems: silicon is tetrahedral cubic (behaves somewhat like body-centered cubic); manganese, like iron, exists in several allotropic forms, and at low temperatures it has a complex lattice that is nearly like body-centered cubic, while at high temperatures it has a face-centered tetragonal lattice that forms solid solutions with gamma (face-centered cubic) iron.

It will be noted that all the body-centered cubic elements are carbide-forming while the face-centered cubic elements are not. Cobalt exists in two allotropic forms. They are not the same as those of iron, however, being more like each other. Silicon forms the carbide Carborundum (SiC) only by high temperature electrolysis. This carbide is not ordinarily associated with steel.

Solubility in the Alpha or Gamma Phase

A third classification, closely related to the second, is based on the relative solubility of the element in alpha or gamma iron. The elements in this classification are tabulated as follows:

More Soluble in Alpha Iron	More Soluble in Gamma Iron
Chromium	Aluminum
Molybdenum	Cobalt
Silicon	Copper
Titanium	Manganese
Tungsten	Nickel
Vanadium	

Effect on Transformation Temperature

The fourth classification will be the effect of the elements on the transformation temperature. This will follow quite closely from the third classification. If an element is more soluble in gamma iron than in alpha iron, it should tend to stabilize the gamma condition and thus lower the temperature at which it changes to the alpha condition. On

the other hand, if it is more soluble in alpha iron it will raise that temperature. It is found that, with the exception of chromium, the elements follow this hypothesis and those that are more soluble in alpha iron (ferrite) raise the transformation temperatures while those that are more soluble in gamma iron lower those temperatures. Chromium is peculiar in that in amounts up to about 12% it lowers the transformation temperatures slightly, but in greater amounts it raises them sharply.

While the theoretical temperatures at which the transformations should occur are affected as stated, there is another effect of special elements that in most heat treatment is more noticeable. That is the effect of supercooling or superheating. This is general for all special elements and means that the transformations will always take place at lower temperatures than in the corresponding carbon steels where practical rates of cooling are applied.

FIGURE 19.1. Effect of special elements on eutectoid ratio (per cent carbon in pearlite). (A) Transformation temperatures for pure iron-carbon alloys. (B) Element lowers A_3. Intersection of A_3 with A_{cm} is shifted to the left. (C) Element raises A_3 but forms carbides that are less soluble than Fe_3C. Intersection of A_3 with A_{cm} is again to the left.

Effect on Eutectoid Ratio

A fifth consideration is the eutectoid ratio, or percentage of carbon in the pearlite. This is nearly always lowered because elements that lower the transformation temperature reduce the solubility for carbon, while those that raise it tend to form insoluble carbides. This might be shown diagrammatically in Figure 19.1.

Effects on Mechanical Properties

The effects described are all the possible effects that can be produced on the equilibrium of iron and carbon by small amounts of other elements. These will show tendencies and explain some of the physical properties obtained in the alloy steels. The carbide-forming elements tend to increase the hardness of steel, due partly to the increased hardness of the carbide itself,[a] but also to the fineness of dis-

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[a] It is probably wrong to assume that the harder carbides make harder steel by virtue of their own hardness. According to the theory of hardness set forth in Chapter XIV, the hardness of steel depends upon the extent to which the ferrite

persion. In alloy steels, with a given cooling rate, the carbides are more finely dispersed than in pearlitic carbon steels. The elements that form solid solutions with the ferrite give increased strength but without loss of ductility. However, since most of the elements are soluble to some extent in both the alpha and gamma phases, the last statement will apply to most of them.

Non-Specific Effects of Alloys

The most important effects of the alloys are general for all of them and are related not to the conditions of equilibrium, but rather to such things as speed of transformation, grain size, and thermal hysteresis. With the carbon steels, great care was necessary in heat treatment to avoid raising the quenching temperature too high above the critical, thereby producing a coarse structure. With the alloy steels, there is less danger of this, and with proper care, finer structures can be obtained than are possible with carbon steel. It was not possible to quench a carbon steel with sufficient rapidity to retain the austenitic conditions at ordinary temperatures. With alloy steels, the structure obtained with any specified rate of cooling will be determined by the amount of special element present. Indeed, with certain steels the condition will be austenitic even when cooled very slowly. Steels are classified as air hardening, water hardening, oil hardening, etc., depending on the rate of cooling necessary to produce martensite.

Effect of Alloys on the Split Transformation

In short, the effect of special elements is to reduce the *rate* at which changes occur. We may recall the phenomenon of the split transformation in which the transformation temperature was progressively lowered as the speed of cooling increased, until it occurred at 600°C. With more rapid rates it occurred in two steps, one between 600° and 550°C, and the other between 300° and 250°C. The diagram for this may be redrawn, with the abscissas representing the percentage of special element instead of speed of cooling (Figure 19.2).

Effect of Carbon Content in Alloy Steels

So far, the effects of the special elements on the carbon steels have been considered. It may be well to look at the subject from the standpoint of varying carbon content on a steel of fixed alloy content. As might be expected, each unit of increase in carbon produces greater

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matrix is prevented from flowing or slipping. However, the harder carbides are also more sluggish in their solution in, or precipitation from, austenite and thus can be controlled more easily to give a finely dispersed precipitate.

changes in physical properties than would be obtained if the steel had no alloy in it. Steels low in carbon are not much different from pure iron even when special elements are present, but as the carbon
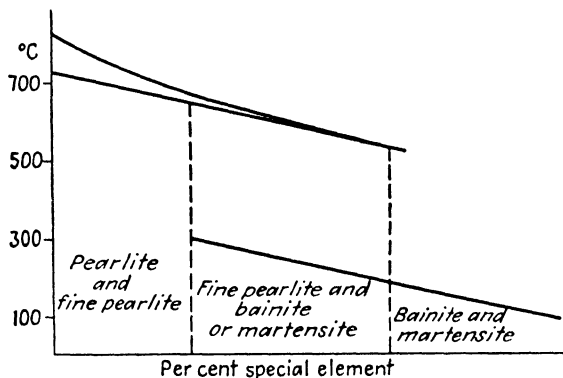
FIGURE 19.2.   Effect of special elements in splitting the transformation into two stages.

increases, the effect of the special element increases. As pointed out before, the eutectoid ratio is usually lower in the presence of special elements so that a lower carbon content is required to give the properties of a eutectoid steel.

Special Effects

The effect of special elements upon grain growth varies but, generally speaking, they reduce it. A few elements, notably aluminum,[4] vanadium, and columbium, are especially effective in this, and steels containing these elements will be fine grained even when high hardening temperatures are used.

Effects of Alloying Elements on the S Curve

The most comprehensive explanation of the effects of alloys in steel generally, as well as the specific effects of the various alloying elements individually, is afforded by the isothermal transformation curves (S curves) which are available now for a considerable number of steels. These make it possible to correlate practically all the metallographic and heat-treating characteristics of these steels and to arrive at a rational understanding of their behavior. When the heat treatment possibilities of any steel are being studied the S curve for that,

[4] Aluminum and vanadium are probably most thought of and used commercially as grain refiners but columbium, titanium, and zirconium are all very effective in minute quantities, and are frequently used.

or a steel of closely similar composition, will be found invaluable as a graphic compilation of related data. It will explain many phenomena, such as hardenability and effects of different quenching media which the more hypothetical split transformation curve does not.

In general, the presence of alloys moves the S curve to the right, indicating a longer time required for the steel to transform at any temperature below A_1. An exception is noted in the case of cobalt which apparently speeds up the transformation and moves the upper part of the S curve to the left. Still other effects are found which are characteristic of the particular alloy and the steel itself, and even of the previous heat treatment to which the steel has been subjected.

These effects are portrayed by the shape of the curve and its position. To simplify the discussion it will be necessary to dwell briefly on the nomenclature that is now applied to different parts of the curve.

Elaboration and Nomenclature of the S Curve

The Ae Points

Since the S curve deals with phenomena that occur at temperatures below that at which austenite is theoretically stable, namely the A_1 point, it is necessary to assume that such a point exists where austen-
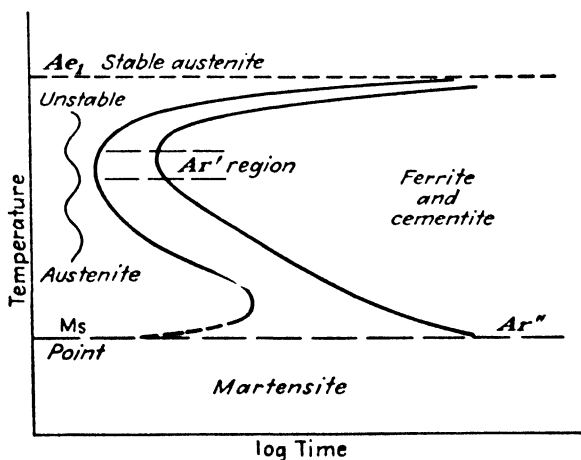
FIGURE 19.3. Nomenclature of subcritical transformation.

ite, ferrite, and cementite are in true equilibrium.[5] This point would be between the Ac_1 and Ar_1 points. For most steels it can be determined with fair accuracy by heating specimens of the steel to a series

[5] Subject to the limitation, of course, that Fe_3C is a metastable compound.

of temperatures between Ac_1 and Ar_1 for sufficiently long periods to secure equilibrium, and then quenching. The first appearance of martensite, or austenite, in the microsection indicates the equilibrium temperature. In connection with S curve studies this equilibrium temperature is called Ae_1.

Similarly, in hypoeutectoid steels, the A_3 point is called Ae_3. The A_2 point is of no significance in these studies.

Now refer to the curve itself (Figure 19.3).

Ar': the Nose of the S Curve

The upper region of rapid transformation, which in most steels occurs between 480° and 595°C is called the Ar' region. This temperature range is critical, in a sense, because above it the product of transformation is lamellar in structure; that is, pearlite and the carbides can usually be resolved by the ordinary microscope; whereas below it the structures are acicular (needle-like) and the carbides, while undoubtedly existent, are submicroscopic (Figure 19.4). The Ar' region is also referred to as the *nose* of the curve.

FIGURE 19.4. Acicular structure, 2000×.

Ar": the Knee of the S Curve; the Ms Point

The lower region of rapid transformation is that in which martensite forms and extends from about 200°C down for carbon steels, the change from austenite to martensite becoming almost instantaneous below 100°C. This is called the Ar'' region (Figures 19.3 and 19.5). The upper limit of the Ar'' region, that is, the temperature at which martensite first starts to form, is called the Ms point.

The Relation of Cooling Rate to the S Curve

The problem of hardenability now becomes a question of cooling with sufficient rapidity so that the time-temperature curve will not intersect the S curve in the Ar' region. Figure 19.6 shows this relationship for four cooling rates.[6] Curves 1 and 2 should result in struc-

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[6] Since the abscissas are logarithmic, the time temperature curves are straighter throughout most of their lengths than when drawn to an arithmetic scale, but bend downward in the higher temperature region.

tures that are wholly martensitic. Curve 3 should produce nodules of fine lamellar pearlite, and pieces cooled as in curve 4 should be completely pearlitic.
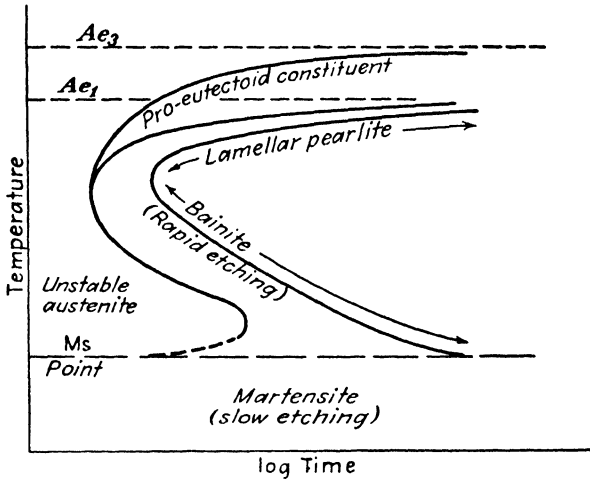
FIGURE 19.5. Structural nature of products of transformation at subcritical temperatures.
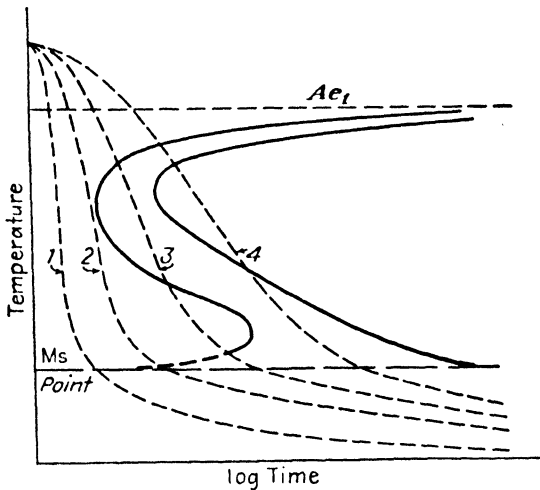
FIGURE 19.6. Relation of time-temperature curves to S curve at various cooling rates.

However, it is not safe to try to predict structures quantitatively from such relations, because the transformation will not, in general, proceed in the same manner under continuously changing temperature as it does at a fixed, subcritical temperature.

In the carbon steels, the only means of producing martensite is by rapid quenching. Indeed, as discussed in Chapter XVII under the McQuaid-Ehn test, some steels cannot be hardened satisfactorily because the "nose" of the curve lies so far to the left that there is no practical way of quenching with sufficient rapidity to avoid some transformation in the *Ar'* region. Furthermore, the size of pieces that can be hardened throughout is very limited, even in normal, coarse-grained, carbon steels, by the heat conductivity of the metal itself.

Specific Effects of Alloys on the Shape of the S Curve

In most of the alloy steels the effect of the alloy is to retard the transformation of austenite at all subcritical temperatures down to *Ar''*.
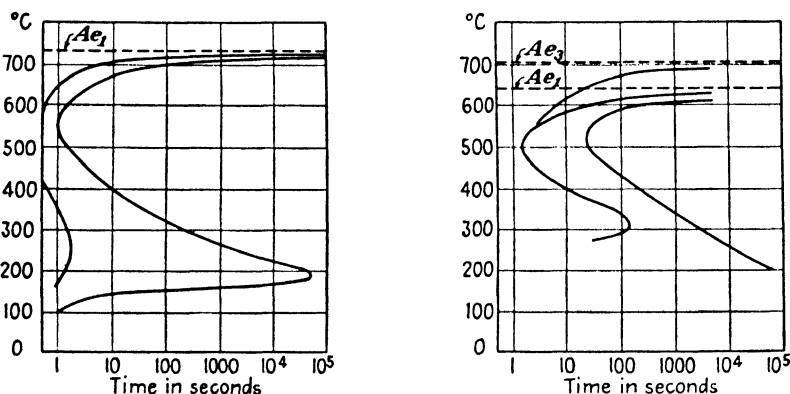
FIGURE 19.7. Left, S curve for carbon steel, 0.59% C, 0.30% Mn. Right, S curve for nickel steel, 0.55% C, 0.33% Mn, 3.88% Ni. (Redrawn from "Isothermal Transformation in Steels," by E. S. Davenport, *Trans. Am. Soc. Metals,* December, 1939.)

However, the extent of the retardation is far from being uniform or related in any simple way to the temperature at which the transformation takes place or the amount of alloy present. Indeed, with many alloy steels, and notably those containing chromium or molybdenum, the shape of the curve is so distorted that it no longer bears any similarity to the letter S.

Many of these S curves have been worked out and published by various investigators,[7] and by concerns that produce or sponsor a variety of steels.[8] However, it should be noted that the intelligent use of such curves requires a knowledge of the conditions under which

[7] "Isothermal Transformation in Steels," by Edmund S. Davenport, 14th Campbell Memorial Lecture, *Trans. Am. Soc. Metals,* December, 1939.

[8] *Atlas of Isothermal Transformation Diagrams,* United States Steel Corporation of Delaware, Pittsburgh, Pa., 1943.

they were obtained. It is important to remember, for instance, that the austenitic grain size prior to quenching affects the transformation rate. Coarse grain decreases it, thereby shifting the curve to the right, whereas fine grain increases it and should cause the curve to be shifted to the left. Ordinarily the austenitic grain size, as determined by the McQuaid-Ehn test or other methods, is noted in connection with the published curves.

An S Curve for Carbon Steel

The curve for 0.59% carbon steel might serve as a standard of comparison for the others. Because of the rapid rate of transformation in the Ar' region the beginning line intersects the left edge of the diagram (Figure 19.7) which represents a holding time of 0.5 second.
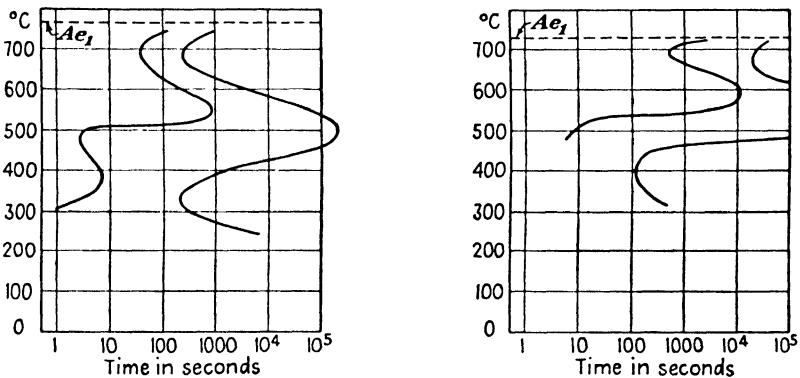
FIGURE 19.8. Left, S curves for chromium steel, 0.32% C, 0.45% Mn, 1.97% Cr. Right, S curves for molybdenum steel, 0.33% C, 0.41% Mn, 1.96% Mo (redrawn after curves by Davenport, *loc. cit.*).

However, this is merely an indication of the difficulties encountered in obtaining results for shorter periods; and from the shape of the curve it would be expected that about 0.3 second would represent the earliest beginning of transformation.

Manganese and Nickel

Manganese and nickel produce effects on the S curve that are closely parallel. The effects of the manganese in various steels containing up to 1.32% manganese are almost identical in every case to the effects of *three times* as much nickel. Thus the shape of the S curve for a 0.65% carbon steel containing 1.32% Mn is very nearly the same in all respects as that of a 0.55% C steel containing 3.88% Ni. In the lower percentage of alloy, one effect of the manganese is to raise the lower

temperature of rapid transformation (Ar'') about 60°C, whereas with the nickel steels little variation of this kind is noted.

With both manganese and nickel the curves for beginning and end of transformation appear to be moved bodily to the right as compared to the corresponding plain carbon steels. However, in evaluating the actual effect of the alloy, it must be remembered that horizontal time values are in a logarithmic series. Thus a 0.30% Mn, 0.59% carbon

Time in seconds for 50% completion of transformation
Steel C 0.88%C; 0.41% Mn; 0.0% V
Steel V 0.90%C; 0.47% Mn; 0.20% V
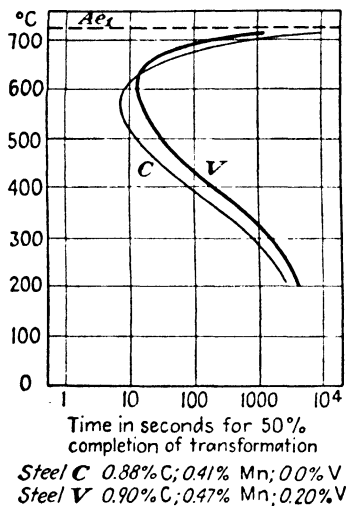
FIGURE 19.9. Effect of vanadium (redrawn from curves by Davenport, *loc. cit.*).

Time in seconds
———— 1.98% Co; 0.98% C; 0.49% Mn
——·—— 0.0% Co; 0.95% C; 0.45% Mn
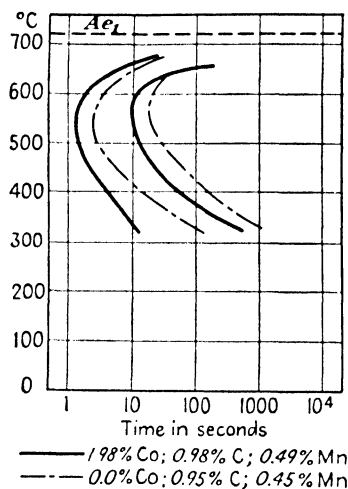
FIGURE 19.10. Effect of cobalt (redrawn from curves by Davenport, *loc. cit.*).

steel begins to transform at 600°C in one-half a second and completes its transformation in about one and one-half seconds; whereas the 1.13% Mn, 0.64% carbon steel shown in the curve begins to transform at 600°C in about four seconds and completes its transformation in about forty seconds (Figure 20.4).

Chromium and Molybdenum

With chromium a new feature appears. This is the bay, or reversal of rapid transformation tendency, right in the middle of the Ar' region. The effect increases in intensity with increasing chromium content and signifies that chromium retards the transformation more in this range of temperature (400° to 600°C) than in any other range (Figure 19.8).

While explanations of this effect are not well established, neither is there any very sound theoretical explanation of any of the fundamen-

tal aspects of the S curves. However, the tendency to form a bay in the Ar' region is characteristic of *strong carbide-forming* elements. It is equally evident in the curves for molybdenum steels.

Strangely enough the speed of transformation is actually increased at higher temperatures by increasing the chromium content, and curves for steels of increasing chromium content start farther and farther to the left at the Ae_1 temperature but cross each other at temperatures between Ae_1 and Ar'. This is true of both beginning and ending curves.

With molybdenum steels the bay ends abruptly at the lower limit of the Ar' region, giving rise to a shelf. Below this shelf the effect of the molybdenum in retarding the transformation is not great.

Vanadium

The effect of vanadium is to move the curve to the right, retarding the transformation, but it also raises the Ar' region so that in the higher temperature levels, that is, near the Ae_1 point, the curve actually lies to the left of the corresponding carbon steel curve, indicating an increased speed of transformation in this range (Figure 19.9).

Cobalt

The anomalous effect of cobalt has been noted in moving the curves to the left. At about 550°C, 1.98% Co reduces the time of start and completion of transformation by about 50% of that for a similar (0.98%C) carbon steel (Figure 19.10).

The Effect of Grain Size on the S Curve

As was noted above, austenitic grain size plays an important part in the position of the S curve, and this effect is interwoven in many cases with the observed effects of the alloys. In general, the smaller the grain size the more is the curve shifted to the left, indicating more rapid transformation. This is clearly in accord with the fact of reduced hardenability in fine-grained steels, since in such steels it is impossible to quench with sufficient rapidity to miss the nose of the curve, as explained on page 218.

Complex Steels

With complex alloy steels, such as SAE steels in which several alloying elements are present, the S curves are characteristic of each steel and, in general, show additive effects of the different alloys present. Nickel and manganese move the curve to the right, as usual, and chromium and molybdenum produce bays and shelves in the Ar' region (Figure 19.11).

Proeutectoid Ferrite

Mention should be made of hypoeutectoid steels. In these the first appearance of proeutectoid ferrite occurs at temperatures below Ae_3. Its rate of precipitation is, like pearlite, increased at lower temperatures.

However, the extent to which it precipitates, before the simultaneous precipitation of ferrite plus carbide (pearlite) sets in, becomes less at lower temperatures until at the lower limit of the Ar' region the proeutectoid precipitation vanishes. This is in accordance with the easily observed fact that rapidly cooled steels usually show no proeutectoid ferrite regardless of carbon content.

The Formation of Martensite

Much has yet to be studied regarding the Ar'' region where martensite forms. Contrary to the early ideas of Davenport and Bain, it is now believed that the formation of martensite depends upon temperature alone.[9] In eutectoid steels it begins to form at some temperature in the neighborhood of 240°C, but the formation proceeds only as the temperature is lowered. The actual transformation to martensite (to the extent that martensite forms) at any one temperature is practically instantaneous; but the amount that forms at that temperature is limited. If the temperature is held constant, bainite will start to form after a period of time that will be represented on a continuation of the S curve. The martensite will not be altered by tempering at temperatures below 200°C, but can be tempered to troostite by reheating to 250°C or higher.

By quenching to room temperature, carbon steel will be converted almost entirely to martensite, but many of the alloy steels will be only partly transformed, and since the formation of bainite is so slow at such temperatures as to be practically inhibited,[10] the steel remains partly austenitic. It has been found that still lower temperatures, down to −150°C, will cause further transformation of this austenite to martensite. This is the basis of recent studies and techniques in *sub-zero treatments* of steel.

[9] "Kinetics of the Austenite to Martensite Transformation in Steel," by Alden B. Greninger and Alexander R. Troiano, *Trans. Am. Soc. Metals,* **28,** 537–563, September, 1940.

[10] It is the author's opinion that the transformation of austenite to bainite can proceed slowly at temperatures below that at which martensite starts to form, and further, that bainite so formed does not have exactly the same structure as the martensite. This is explained on the principle that the formation of bainite is dependent upon a certain amount of carbon diffusion through the austenite, whereas the formation of martensite requires only a change of space lattice.

The *Ar″* temperature, at which martensite will start to form, is indicated in Figure 19.3 (on page 215) by a dashed line.

Equilibrium in Systems of More than Two Components

While the S curve is of great value in the understanding and correlation of structures produced by subcritical transformation, we cannot dismiss the equilibrium relations entirely. Here the phase rule calls attention to some effects of three or more components that modify some of the ideas derived from binary diagrams. In the binary systems it was found that eutectics, peritectics, eutectoids, and the like were invariant points where changes were completed under equilibrium conditions with no change in temperature. Here the number of phases was three, so that for two components

$$F = 2 - 3 + 1 = 0.$$

Now consider a three-component system where a solid solution (austenite) is in equilibrium with two solid phases simultaneously, namely, ferrite and cementite. Applying the phase rule:

$$F = 3 - 3 + 1 = 1.$$

FIGURE 19.11. Subcritical transformation curve for SAE 4640: 0.36% C, 1.8% Ni, 0.2% Mo (redrawn after curves by Davenport, *loc. cit.*).

This means that under equilibrium conditions a two-phase structure such as pearlite will form from austenite, not at a constant temperature but through a range of temperature, and the compositions of some of the phases will vary as the temperature changes. Such a condition is not, strictly speaking, a eutectoid point, but the structure formed may resemble eutectoid structures.

Thus, with steels containing nickel or manganese, the effect of the alloy is to lower the temperature at which austenite transforms. But the ferrite that forms on cooling will not, in general, contain the same per cent of the alloy as the austenite. This is also true of the carbide phase so that the composition of the austenite will change while both ferrite and carbides are forming.

Figure 19.12 shows a section through the transformation ranges of the ternary nickel- and manganese-iron-carbon diagrams. Note the close similarity in effect of manganese and nickel. The region labeled $F + A + C$ represents the compositions and temperatures of alloys that, under equilibrium conditions, will be composed of ferrite, austenite, and carbide phases. We cannot, however, apply the lever law or the rules for determining phase compositions to this diagram because the lines do not necessarily represent the compositions and temperatures of phases that are in equilibrium with *each other.*
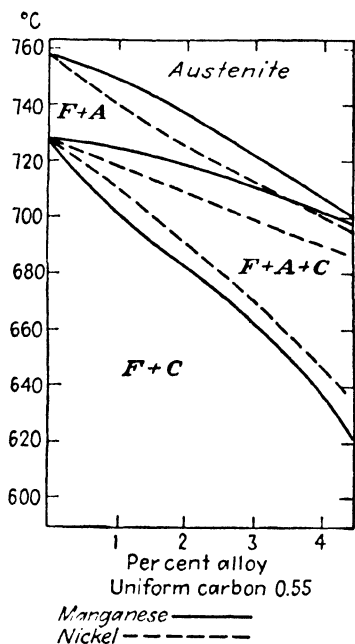
FIGURE 19.12. Section through the iron-(manganese or nickel)-carbon ternary diagram at 0.55% carbon. (From "On The Rate of Reaction in Solid Steel," by E. C. Bain, *Trans. Am. Inst. Mining Met. Engrs.*, 100, 13, 1932.)

Partial Transformations

Because of the effects just noted it is frequently possible for the austenite in a nickel or manganese steel to start transforming at a subcritical temperature and proceed until the remaining austenite reaches a composition that is stable for that temperature. At this point the transformation ceases and some austenite will remain indefinitely or until there is a further reduction in temperature.

With nickel steels there is a further complication resulting from the fact that nickel promotes the tendency of carbon to precipitate as graphite. However, the time required for this is greater than that employed in most heat treatments.

Commercial Alloy Steels and Specifications

The actual compositions and specifications for various steels are so numerous as to defy complete classification. The Society of Automotive Engineers (SAE) [11] and the American Iron and Steel Institute (AISI) have published lists of standard specifications. These specifications include physical property charts and tables that give average values of physical and mechanical properties that should be looked for in each composition range.

[11] *SAE Handbook,* 1942, Society of Automotive Engineers, Inc.

The specification numbers are so selected that they give an indication of the composition limits. The first digit indicates the type of alloy steel; thus 1 indicates a carbon steel, 2 a nickel steel, and so on. The second figure indicates very roughly the percentage of alloy present, or sometimes classifies the steel as to some other quality, such as free machining characteristics, resistance to corrosion, and the like. The last two or three digits express a value near the middle of the carbon range. This range varies from about 0.05% in low-carbon steels to 0.15% in high-carbon steels.

In lists published prior to 1942, the letter X in front of SAE numbers indicated that the analysis had been modified for special purposes. Since then the X numbers have been replaced with numbers that fit into the general classification.

Numerous publications contain lists of these specifications and specification numbers.[11-14] The AISI numbers are quite similar to the SAE numbers but letters are prefixed to the AISI numbers to indicate the method of manufacture.

The classification of SAE specifications with respect to the different alloys is as follows:

Type of Steel	Range of SAE Specification Numbers
Carbon	1008 to 1095
Free cutting	1111 to 1145
Manganese	1320 to 1340
Nickel	2317 to 2515
Nickel-chromium	3115 to 3310
Chromium	5210 to 52100
Molybdenum	4023 to 4820
Chrome-vanadium	6150
Silicon-manganese	9260
Stainless chromium	51210 to 51710
Chrome-nickel (austenitic)	30615 to 30915

In the AISI classification the letter prefixes are as follows:

A. Basic open-hearth alloy steels.
B. Acid Bessemer carbon steels.
C. Basic open-hearth carbon steels.
CB. Optional, acid Bessemer or basic open-hearth steels.
D. Acid open-hearth carbon steels.
E. Electric furnace alloy steels.

In addition to the SAE and AISI classifications there are also the national emergency (NE) steels. Some of these were developed to

[12] *National Metals Handbook*, American Society for Metals, Cleveland.
[13] *Metals and Alloys Data Book*, by S. L. Hoyt, Reinhold Publishing Corp.
[14] *Mechanical Properties of Metals and Alloys*, Bureau of Standards, Circular C447.

meet special war demands, and others to circumvent critical shortages in some of the alloying elements, notably nickel and tungsten. Information regarding the NE steels is available in *Metals and Alloys Data Book*[13] and from the American Society for Metals.[15]

QUESTIONS

1. Which of the alloying elements are eliminated completely or almost completely by oxidation if they are present in the early stages of the steelmaking process, and which are not eliminated?

2. Is there any relationship between the oxidizability of these elements and their carbide-forming tendencies?

3. Would you expect the effect of the alloy on physical properties to be greater in annealed or in heat-treated steels? Explain.

4. If a three-component solid solution is in equilibrium with a liquid of a given temperature and composition, should the exact composition of the solution be determinable from a three-component diagram? Explain.

5. What is the per cent of carbon in each of the carbides whose formulae are given on page 210?

6. Name an outstanding characteristic of tungsten carbide.

7. Name an outstanding use for tungsten metal (not in steel).

8. In which alloy steels should it be possible to produce a bainite structure by continuous cooling?

9. How would you expect the disappearance of proeutectoid ferrite, in steels transformed below the Ar_1 temperature, to affect the distribution of carbides?

10. What is the principal effect of vanadium? Are vanadium steels abnormal? Have they good hardenability?

[15] *National Emergency Steels,* American Society for Metals, 1942.

Specific Characteristics of Nickel Steels and Manganese Steels

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Nickel Steels · The Iron-Nickel Equilibrium Diagram—Irreversible Alloys · Effect of Nickel on Mechanical Properties · High-Nickel Alloys · Manganese Steels · The Iron-Manganese Equilibrium Diagram · The S Curve for Manganese Steel · Effect of Manganese on Mechanical Properties · Other Effects of Manganese

Nickel Steels

Composition Range

Nickel steels may contain from 0.5% to more than 5% nickel; 3.5% nickel with a variety of carbon contents being the favorite for forging and heat treating. Carburizing steels may contain 2% to 5% nickel and the austenitic stainless steels are standardized at 8% nickel with 18% chromium.

The Iron-Nickel Equilibrium Diagram—Irreversible Alloys

The iron-nickel equilibrium diagram (Figure 20.1) is typical of alloys of iron with metals that crystallize in the face-centered cubic lattice. Note the peritectic point involving the delta-gamma change. This indicates that nickel, like carbon, dissolves in austenite and increases its stability with respect to the body-centered delta phase.

Likewise, and for the same reason, the temperature of the gamma-alpha (or gamma-beta) change is lowered. Because of the sluggishness of the transformation in iron-nickel alloys it has been very difficult to determine the critical points with high accuracy, and most published diagrams have shown the approximate locations of the changes at practical rates of heating and cooling with appropriate

nomenclature, for instance, $\alpha + \gamma$ (heating) and $\alpha + \gamma$ (cooling) as in Figure 20.1. Because the hysteresis gap is so wide, it is possible to produce nickel steels that, upon rapid cooling, will remain austenitic apparently indefinitely or, with less rapid cooling, will be ferritic (martensite). This has given rise to the term *irreversible alloys*. The criterion of reversibility is whether or not the steel will transform to martensite when quenched. If it can be kept entirely austenitic it is said to be irreversible.

Probably the nearest approach to a true diagram in the critical range is the one by Jette and Foote [1] shown in Figure 20.2. Although this shows but four points on the alpha solvus curve and but two on the gamma solvus, the methods employed and the quality of the work done leave no doubt as to the accuracy of the results. The true curves can be assumed to lie within the shaded bands.

From the diagram [2] it can be assumed that at 400°C

FIGURE 20.1. The iron-nickel equilibrium diagram (tentative; transformations for practical heating and cooling rates).

ferrite is the stable phase in alloys containing less than 6% nickel, and austenite is stable in alloys containing more than 40% nickel. Between these two values, stable alloys should consist of two phases.

Since most nickel alloy steels for structural purposes contain less than 5% nickel, it is apparent from both Figures 20.1 and 20.2 that such steels are ferritic at ordinary temperatures. Therefore, they become martensitic when quenched and behave generally in a manner similar to carbon steel except when the rate of cooling necessary to produce martensite is reduced by the presence of the nickel. The S curves for these steels (Figure 19.7) also bear out this deduction.

[1] "An X-Ray Study of Iron-Nickel Alloys," by Eric R. Jette and Frank Foote, *Trans. Am. Inst. Mining Met. Engrs., Iron and Steel*, Tech. Pub. 670 (1936).
[2] Since the atomic weights of iron and nickel are not far apart, atomic per cent and weight per cent are nearly the same in the range of composition of this diagram.

Effect of Nickel on Mechanical Properties

The effect of nickel on the physical properties depends in a rather complicated way on the carbon content, the composition with respect to other elements, and the actual heat treatment employed.

To illustrate: the effect of 5% nickel on carbonless iron in the annealed condition is comparatively low [3] in regard to tensile strength.

In the normalized (air-cooled) condition, the tensile strength and yield point are about 25% higher for the nickel alloy than for the pure iron. Elongation and reduction of area values are also a little higher for the nickel alloy. As carbon is added, the tensile strength runs from 15 to 20% higher than in the corresponding carbon steels, while the yield point may rise to 35% higher at 0.20% carbon. These increases are reduced a little at higher carbons. Again, nickel steels, even in the higher carbons, show small increases in elongation and reduction of area over the corresponding carbon steels.

So far, these effects can be attributed to the solution of the nickel in the ferrite where it acts as a strengthener and grain refiner.

When a carbon-nickel steel is heat-treated the full extent to which the

FIGURE 20.2. Iron-nickel equilibrium in the critical range (from "An X-Ray Study of Iron-Nickel Alloys," by Eric R. Jette and Frank Foote, in *Trans. Am. Inst. Mining Met. Engrs.,* 1936).

nickel can affect the tensile properties becomes manifest. This is best shown in the table on page 230.[4]

Here the greatly increased tensile and yield values must be attributed to the effect of the nickel on the distribution of the carbides. The lower temperature required for quenching the nickel steel and the retardation of the transformation at Ar' (whereby the S curve is shifted to the right) result in a sound martensitic structure. The sluggishness of reactions in the ferrite at the tempering temperature is responsible for the finer sorbitic structure necessary to give such

[3] *Steel and Its Heat Treatment,* by D. K. Bullens, revised by the Metallurgical Staff of the Battelle Memorial Institute, fourth edition, Vol. II, Chapter 6, page 113, John Wiley and Sons.

[4] Compiled from *Steel and Its Heat Treatment,* Bullens-Battelle, cited in the footnote preceding.

	0.26% C without Ni	0.30% C, 3.5% Ni
Quenched:		
In.....................	Oil	Oil
From....................	1650°F	1450°F
Tempered to............... .	1025°F	1050°F
Tensile strength, psi..........	77,210	125,000
Yield strength, psi...........	52,200	110,000
Elongation in 2 in., %........	28	22
Reduction in area, %........	65	62

high tensile values. However, the effect of the nickel in the ferrite is clearly shown in the well-maintained elongation and reduction of area.

The fatigue limit is somewhat improved in nickel steels although this is probably the direct result of the increased tensile and yield values.

Nickel greatly improves the *impact strength* of steel. This would seem to be in keeping with the increased strength without lowered ductility. Nickel steels are thus popularly characterized by their *toughness*.

High-Nickel Alloys

Besides the steels of the low-alloy class that have just been discussed, there are a number of special alloys of iron and nickel in high concentration. These contain little or no carbon, as nickel over 5% has an increasing tendency to promote graphitization, thereby throwing the carbon out of solution.

Invar

The first of these special alloys goes by the name *invar*. It contains 36% nickel and 64% iron. Its outstanding characteristic is a coefficient of expansion close to zero between room temperature and 100°C. While the exact cause of this property is not definitely established, it seems likely that it is in some way connected with the gamma-alpha change which is close to room temperature for this composition.

Invar is used in the manufacture of instruments where exact dimensions must be maintained in spite of fluctuating temperature. Another application was found in the use of aluminum pistons for internal-combustion engines. The high expansion coefficient of the aluminum made it impossible to maintain close fits in gray iron cylinders until a way was found to compensate for this expansion by an invar strut or tie bar.

Platinite

As the nickel content is increased above 36% the expansion coeffi-
cient increases gradually. Such alloys have high corrosion resistance
and structural stability. In incandescent light bulbs the filament is
supported by heavier electrodes which must pass through the glass to
the outside of the evacuated bulb. At one place the glass is fused
around these electrodes. This practice demands a metal that will not
crack the glass when it is cooled, and for several years platinum was
the only metal used for this purpose. However, a cheaper material was
imperative if electric lights were to be used universally; and the alloy
of 46% nickel and 54% iron, which had the same expansion coefficient as
platinum, was used with success. This alloy is called *platinite*. A 42%
nickel wire coated with copper, known as Dumet, now seems the most
satisfactory for this purpose.

Permalloy

The magnetic character of nickel has been known for many years,
but it was considered far inferior to iron until the discovery of *permal-
loy*. A glance at the iron-nickel equilibrium diagram Figure 20.1 shows
the magnetic change in austenitic (face-centered cubic) iron-nickel
alloys to occur at a maximum temperature in the vicinity of 78.5%
nickel.

Permalloy is remarkable in having the highest magnetic permeabil-
ity at low field strengths of any known substance, which means that in
the presence of a moderately intense magnetic field it becomes magne-
tized almost to the full strength of the field. It has low retentivity,
which means that there is very little magnetism left when the field
is removed, and when properly produced or fabricated its magnetic
hysteresis is practically zero.

Permalloy is very useful for transformer cores, especially in radio
work where the effect of hysteresis is to distort the signal.

Many other magnetic alloys of iron and nickel are available with
properties adjusted to specific types of service. With the further addi-
tions of aluminum, cobalt, chromium, or tungsten, permanent magnets
of great strength are made. These, of course, have high retentivity.
They are usually heat treated either by ordinary quenching and tem-
pering as in the case of the tungsten-cobalt steels, or by precipitation
of complex phases as in the iron-aluminum-nickel-cobalt alloys.

Manganese Steels

After a brilliant start as an essential addition in the manufacture of
steel, as explained in Chapter XII, manganese has never quite come

up to expectations as an alloying element. Possibly this is because too much has been expected of it, but a probable explanation is that its most striking effects have always been taken for granted as part of the essential characteristics of carbon steels. It must be admitted that all commercial carbon steels are, in reality, iron-carbon-manganese alloys, and the physical properties and microstructures with which we are so familiar, and which we so definitely relate to the carbon content, are quite different from those that would be found in manganese-free alloys. Thus, in dealing with manganese alloy steels, we are noting only the effects of increased amounts of that element which is already present.

Tabulation of the various effects of manganese would indicate that it is the perfect alloy for steel (which it certainly is not) and that it should convey to steel most of the good qualities of other alloying elements. It lowers the critical temperatures in a manner almost identical to nickel (Figure 19.12). It is a carbide-forming element, but is also soluble both in ferrite and austenite. It moves the S curve to the right in a manner similar to nickel but requires about one-third as much manganese. It increases depth of hardening and improves case carburizing properties.

Yet, its effects are quite limited in extent and the quantity used in heat-treated steels cannot exceed about 2% because of a serious embrittling effect. This, of course, does not apply to the austenitic manganese steels with 12% or higher manganese.

Probably the most important reason for the use of manganese is its cheapness. Next to carbon it is the cheapest alloy that can be used to increase the strength of steel. Like some of the other alloys, it does not, however, reduce the need for care in heat treating and close control of quenching temperature. Much manganese steel is used in an unheat-treated condition and such steels show good strength on air cooling.

Composition Ranges

The compositions of manganese steels range from about 0.8% manganese (upper limit for carbon steels) [5] to 2%. Favorite compositions are around 1%, 1.25%, 1.65%, and 1.90%. The embrittling effect is related to both manganese and carbon so that as the manganese is increased the carbon should be lowered. Carbon content of 0.40% with 1.50% manganese represents an upper limit, and if one is increased the other should be decreased in about the same proportion of the

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[5] However, there is no definite composition that distinguishes carbon steels from manganese steels.

amount present. Thus with 0.30% carbon, 1.85% manganese might be used successfully.

The Iron-Manganese Equilibrium Diagram

Some of the effects of manganese are best understood by reference to the iron-manganese equilibrium diagram (Figure 20.3).

Manganese exists in three allotropic forms.[6] The alpha form has a complex modification of the body-centered cubic space lattice involv-
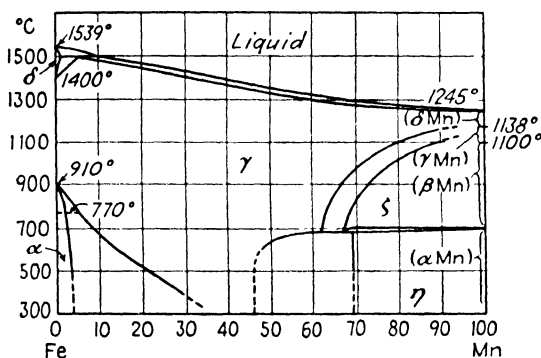
FIGURE 20.3. The iron-manganese equilibrium diagram (redrawn with alterations from *National Metals Handbook*).

ing 58 atoms per unit cube. The beta form is complex cubic with 20 atoms per unit cube. The gamma form is tetragonal and, as seen in the diagram, forms a continuous series of solid solutions with gamma iron. In the series, the space lattice is face-centered cubic up to about 70% manganese and tetragonal above this amount.

A tetragonal lattice may be considered as either face centered or body centered, depending upon how the axes are chosen. Thus, the face-centered tetragonal lattice of manganese must be very similar to the face-centered cubic lattice of gamma iron but distorted in one axial direction. Up to 70% manganese the iron can apparently completely suppress this distortion, but above 70% the manganese distorts the iron lattice.

Again, manganese is soluble in alpha iron up to at least 10% at temperatures below 600°C, but, in this range of temperature, iron has a body-centered cubic lattice whereas manganese, by itself, exists in a *modified* body-centered cubic lattice. One might look to these lattice differences for explanations of some of the peculiarities of manganese

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[6] A fourth, or delta, form is assumed because of an arrest in the cooling curve at 1138°C. It has not otherwise been distinguished from the gamma form.

steels. Particularly, they might explain the fact that ductility is not maintained in manganese steels as well as it is in the nickel steels and also the serious problem of warpage in manganese steels.

The S Curve for Manganese Steel

The S curve for manganese steel shows its similarity to nickel in retarding the subcritical transformations.

Effect of Manganese on Mechanical Properties

The evidence presented so far might be taken to indicate that manganese steels should have similar properties to nickel steels with the increased hardening effects of a carbide-forming element thrown in for good measure. Yet it falls far short of this desirable goal for reasons that are obvious enough. In the first place, the increase in strength due to solid solution in the ferrite is not accomplished without loss in ductility. Second, the carbide formed (Mn_3C) is not much different in hardness from iron carbide (Fe_3C), and consequently its effects are not striking.
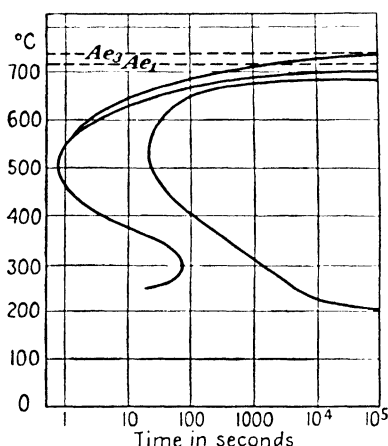
FIGURE 20.4. S curve for a manganese steel, 0.64% C, 1.13% Mn, grain size 7. Compare with Figure 19.7. (Redrawn from "Isothermal Transformation in Steels," by E. S. Davenport, *Trans. Am. Soc. Metals*, December, 1939.)

What, then, are the advantages to be found in manganese steels? The answer depends upon the use to which the steel is put. There is an increased yield strength with ultimate strength similar to carbon steel. This is accomplished, presumably, with a reduction in carbon as the manganese is increased. The result is a tougher steel with higher impact value than would be found in a carbon steel of the same ultimate strength.

Other Effects of Manganese

Manganese improves the normality in steels and produces larger austenitic grains. This makes for better case-carburizing properties and better hardenability. It makes a favorite alloy for large castings that are difficult to harden deeply. It improves machinability, partly because of its effect in producing more normal pearlite, and partly

because of its effect on dissolved sulphides and oxides. These have lower solubility in the presence of manganese and this causes them to form spheroidized particles which, without seriously reducing the strength, allow the metal to form chips easily in cutting. SAE specifications for steels having high manganese and sulphur indicate free-machining steels. They apply to steels containing less than 0.25% carbon because steels of higher carbon content than this are machined easily without addition of other elements.

To recapitulate: The outstanding advantages of manganese in the low-alloy steels are (1) cheapness, (2) increased hardenability, (3) better carburizing properties, (4) increased yield strength without loss of ductility, possibly accounting for a somewhat higher impact value, (5) permitting an increase in sulphur and thuŝ giving improved machinability. These are partially offset by: first, a tendency toward brittleness if the carbon is high; second, coarse grain size requiring special treatment to secure grain refinement; and third, increased warpage in heat-treated and carburized parts.

QUESTIONS

1. Can you explain why, in the diagram of Figure 20.1, the shaded area labeled "$\alpha + \gamma$ (heating)" ends abruptly at about 36% nickel. *Note:* Consider the Jette and Foote diagram of Figure 20.2.

2. Metallic meteorites are composed of iron with about 7% nickel and practically no carbon. The Widmanstätten structure observed in these is composed of what two phases?

3. In a carburizing steel, what should be the effect of nickel in the case and in the core?

4. Is it advantageous to be able to produce martensite with moderate cooling rates? Why?

5. To give good machinability, the manganese specification is raised for low-carbon steels in which the sulphur is high. What is the purpose of the extra manganese?

6. Rail steels may contain 0.70% carbon with 0.80% manganese. Does this carbon-manganese ratio seem high or low?

7. Should an increased yield strength relative to ultimate strength, with similar values for elongation, account for higher impact values in manganese steel?

8. How should coarse grain size in manganese steel affect the S curve?

Specific Characteristics of Chromium Steels and Molybdenum Steels

Chromium as an Alloying Element

Next to carbon, chromium is probably the most effective single element used in steel. Ranking next to manganese in cheapness, it can improve the physical properties of steel in so many different ways that it is undoubtedly the greatest favorite in the making of alloy steels. However, today, chromium is almost always used with other alloying elements because it seems to enhance their effects, and its effects are likewise enhanced. Thus we have chrome-nickel, chrome-vanadium, chrome-tungsten, chrome-molybdenum, and many more, in addition to the more complex steels using chromium as one of the important alloying elements.

General Effects of Chromium

To understand the effect of chromium it may be well to study first the chemistry of the element itself. It is a high potential element. That is,

it forms oxides, sulphides, and other such compounds with great evolution of heat, somewhat greater than manganese although less than silicon. Thus, it is a good deoxidizer and although it would not be used intentionally for such a purpose, it would be expected to help clean up any small residual oxidation after other deoxidizers have been used. The oxide of chromium is a very high melting refractory which does not fuse readily with either acid or basic refractories. This, in part, accounts for the ability of chromium to render steels stainless.

Chromium can, to a certain degree, combine with atmospheric nitrogen at high temperatures. This may have some connection with some of its unusual hardening effects.

As noted in the early part of Chapter XIX, chromium is a carbide-forming element. Unlike manganese, it forms very hard carbides which make it valuable in improving resistance to abrasion.

The Carbides of Chromium

The composition of the carbides depends upon the amount of carbon and chromium present. With less than 2% chromium the cementite of the pearlitic steels is Fe_3C, with some chromium probably replacing iron. With higher chromium or lower carbon, Cr_7C_3 forms. This has a different crystal lattice from Fe_3C and may contain some iron in place of chromium. With still higher chromium or chromium-carbon ratios, Cr_4C will form with more or less iron. The higher chromium carbides seem to be much harder than cementite and more sluggish in solution in, or precipitation from, austenite.

Space Lattice Chromium and the Iron-Chromium Equilibrium Diagram

The space lattice of chromium is body-centered cubic and it apparently undergoes no allotropic changes between room temperature and its melting point. Its lattice dimensions are very close to those of alpha (body-centered) iron. The iron-chromium equilibrium diagram (Figure 21.1) shows its compatibility with the various forms of iron.

It is this diagram that confirms the structural identity of alpha, beta, and delta iron. Accordingly, alloys containing more than 12.8% chromium undergo no structural changes when cooled from their melting temperatures, and alpha, beta, and delta iron form solid solutions in all proportions with chromium.

The range of stability of the gamma phase presents a feature in equilibrium diagrams not hitherto discussed. This is a minimum point in solid solubility relationships. Recalling that a region of heterogeneity must always separate horizontally two regions of homogeneity (in

this case the gamma region from the beta-delta region) the solvus curves bounding the two regions must be tangent at the point of lowest transformation temperature. This is strictly in accord with equilibrium principles and is not surprising inasmuch as the liquid-solid relationships also show a minimum point. It illustrates and accounts for the statement, made at the beginning of Chapter XIX, that with small amounts of chromium the transformation temperatures are lowered, but rise sharply with larger amounts.

The shape of the gamma field in this and other systems of iron with body-centered or ferrite soluble elements suggests the term "gamma loop." Alloys whose compositions lie within the range of the gamma loop are hardenable by quenching.

FIGURE 21.1. The iron-chromium equilibrium diagram (redrawn by permission from *The Alloys of Iron and Chromium,* Kinzel and Crafts, copyright, 1937, by McGraw-Hill Book Co., Inc., page 3).

The effect of carbon is to increase the solubility of chromium in the gamma phase (austenite), thus expanding the gamma loop. This works in all directions, that is, as in carbon steels, the temperature of the delta-gamma change is raised and that of the gamma-alpha change is lowered, by raising the carbon content. Thus carbon and chromium may be said to oppose each other in their effects on transformation temperatures.

As long ago as 1927 Bain and Griffiths [1] noticed a brittle constituent in chromium-iron alloys containing between 30% and 55% chromium. This has been named the B constituent, the X constituent, and finally the sigma phase. It appears in pure iron-chromium alloys after long sojourns at temperatures below 900°C. In the presence of nickel or when the alloy is cold worked this phase forms more rapidly. Its existence is now well established in the iron-chromium system. Its composition is FeCr.

The Low-Chromium Steels

In the range of chromium content up to 5%, chromium acts as a ferrite strengthener in a manner similar to, but not as effective as,

[1] E. C. Bain and W. E. Griffiths, "An Introduction to the Iron-Chromium Nickel Alloys," *Trans. Am. Inst. Min. Met. Engrs.,* 1927, **75,** 166.

nickel. In this range it also acts as a carbide former much more effectively than manganese, forming with iron a rather complex series of carbides and double carbides, whose compositions depend on the amount of chromium and carbon present. As mentioned, these carbides are harder than iron or manganese carbide.

In addition to these desirable effects, chromium greatly reduces the speed of solution of the carbides in austenite and makes all the transformations more sluggish. This is clearly indicated by the shape of the S curve (Figure 19.8). The shift of the curve to the right is noted for all temperatures and the deep bay where the Ar' region might be expected (compare Figure 19.3) indicates a greatly reduced rate of pearlite formation. While there is no complete explanation as yet for this bay in both chromium and molybdenum steels, it seems very probable that it is related in some way to the formation of complex carbides.

Straight Chromium Steels

Straight chromium steels for structural purposes are rather limited in number. The following SAE specifications are representative. Number 5120 is a favorite carburizing grade and 52100 is used chiefly for ball and roller bearings.

SAE number	% C	% Mn	% Cr
5120...........	0.15–0.25	0.30–0.60	0.60–0.90
5140...........	0.35–0.45	0.60–0.90	0.80–1.10
5150...........	0.45–0.50	0.60–0.90	0.80–1.10
52100..........	0.95–1.10	0.20–0.50	1.20–1.50

With up to 2% of chromium the steel should remain pearlitic on air cooling. However, the carbon content affects this characteristic and, with increasing carbon contents, there is a tendency for steels containing even less than 1% of chromium to form bainite and thus rate as air hardening. With up to 0.50% chromium and 1.00% carbon, the increase in tensile strength due to the chromium may be as high as 15 or 20% with practically no loss in ductility. Above 1.00% chromium the ductility begins to drop. Where such high percentages of chromium seem desirable, it is customary to specify the more complex steels which use a ferrite strengthening element such as nickel in addition to the chromium.

The effect of chromium in the heat-treated steels is complex, and to understand it one must consider several factors. First, the sluggishness

of precipitation of the carbide increases hardenability. In this, chromium is as effective as manganese, or even more so. However, sluggishness of solution of the carbides on heating makes this hardenability sensitive to, and increase with, the temperature of heating. Second, the effect of undissolved carbides is usually to reduce grain size, which in itself tends to reduce hardenability. The net effect is increased hardenability, however, and much of the value of chromium lies in its ability to maintain hardenability in fine-grained steels.

Stainless Steels

The ability of chromium to render steels corrosion resistant, or "stainless," is of interest. Actually, the so-called stainless steels are iron-chromium or iron-chromium-nickel alloys, so different from ordinary steels that they should probably be considered separately. Two principal types of these steels are used although there are many other variations.

The well-known "18 and 8" is an iron-chromium-nickel alloy containing 18% Cr; 8% nickel; usually less than 0.10% carbon; the balance iron and impurities. It is not amenable to heat treatment, other than annealing after cold work, and has good tensile properties for a structural steel.

Heat Treatment and Stainless Steels

The other type is sometimes called the cutlery type and may contain 12 to 17% chromium and carbon in amounts varying from 0.10 to over 1.00% with no nickel. This type can be hardened and tempered. Many variations of this latter material are now available and there are numerous high-chromium iron alloys containing other alloying elements, but the cutlery type will serve to illustrate the principles involved in their heat treatment.

Because of the high chromium, the gamma range is restricted so that the austenitizing temperature must be high (but not too high) for fear of encroaching upon the delta region. This is illustrated in the diagrams (Figure 21.2) from Krivobok and Grossmann.[2]

Complete solution of the carbides requires much longer time in this restricted temperature range than would be required for carbon or low-alloy steels. As an illustration: A 14% Cr, 0.35% C alloy in thin sheets required thirty-five minutes at 1800°F for complete solution of its carbides which were coarsely spheroidized prior to heat treat-

[2] "Influence of Nickel on the Chromium-Iron-Carbon Constitutional Diagram," by V. N. Krivobok and M. A. Grossmann, *Trans. Am. Soc. Steel Treating*, **18**, 808 (1930).
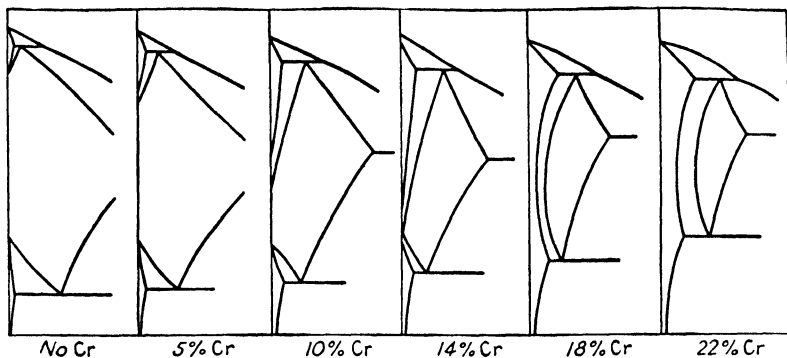
FIGURE 21.2. Hypothetical sections of ternary iron-chromium-carbon equilibrium diagram at successively higher percentages of chromium (after Krivobok and Grossmann).

ment. The actual time will, in any case, depend upon the coarseness of the carbide particles. This same steel, after hardening, was tempered at 1100°F whereupon it showed a black troostite structure with no distinguishable carbide particles. In this condition less than one minute at 1800°F resulted in complete austenitization.

Corrosion Resistance of Stainless Steels

The corrosion-resistant or stainless properties of the high-chromium alloys depend on chromium in solid solution. Chromium as carbide does not render the steel stainless. In the case of the "18 and 8," the nickel, plus the chromium, keeps the steel austenitic at ordinary temperatures. No carbides are formed, and so the full effect of the chromium is realized. In the case of the heat-treatable alloys, increased physical properties are secured as a result of precipitated carbides in a ferrite matrix. These carbides, however small, rob the ferrite of chromium so that unless the ratio of chromium to carbon is high enough to leave 8 to 10% Cr in the ferrite, the steel will not be stainless after tempering. Of course, in the martensitic or austenitic condition the same steel would be stainless.

The mechanism by which chromium renders steel stainless seems to lie in the formation of an impervious protective coating of oxide of iron and chromium. This can occur only in solid-solution alloys where the chromium is distributed atomically in the space lattice.

We may summarize the effects of chromium by stating that it increases strength and hardness without loss in toughness, increases hardenability without coarsening of grain, and in high percentages renders iron alloys stainless and corrosion resistant.

Molybdenum Steels

Molybdenum has been used as an alloy in steel for nearly as long a time as its sister element tungsten. For reasons of cost, trade prejudice, and lack of knowledge regarding its use it was less popular than tungsten until the approach of World War II. Its promoters and producers had labored persistently to educate the trade to its advantages but with meager success. Yet, if a metal were to be chosen as most representative of the developments and advances in alloy steels during the war period, this author's vote would go without qualification to molybdenum.

Critical shortages of many alloying elements in the face of enormously increased steel production had made the reduction of alloy content imperative. Nickel, which had been used so generously during peacetime, could not be produced in sufficient quantity to meet wartime demands. Tungsten importations, uncertain even in peacetime because of transportation difficulties in China, were practically cut off. Without high-speed steel tools, war production would have faced disaster. Chromium, manganese, and vanadium were plentiful but by themselves incapable of producing all the necessary qualities in steel.

Molybdenum, pound for pound about twice as effective in changing the properties of steel as tungsten, came to the rescue handsomely and the United States was fortunate indeed to have the world's most important supply within its own borders.

Effects of Molybdenum

To a yet greater degree than chromium, molybdenum produces its greatest effect in combination with other elements. However, the specific improvements in steel that are attributable to molybdenum alone may be listed as follows:

1. Molybdenum increases the usable strength in steel. It is difficult to secure a plain carbon steel that can be heat treated to a tensile strength of over 175,000 psi without becoming too brittle for most constructional service. With molybdenum this limit is raised to about 275,000 psi.

2. Molybdenum increases depth of hardening, that is, hardenability.

3. Molybdenum increases high-temperature strength and resistance to "creep."

4. Molybdenum eliminates "temper brittleness."

5. Molybdenum increases impact strength.

6. Molybdenum induces "secondary hardness" in high-speed steels.

Corrosion Resistance of Molybdenum Steels

While molybdenum improves the corrosion resistance and resistance to oxidation of the high-chromium austenitic stainless steels, it has the opposite effect in pearlitic steels. Pearlitic steels containing molybdenum are especially given to surface decarburization during heat treatment. Originally it was thought that the high volatility of molybdenum oxide resulted in loss of molybdenum by surface oxidation. Later this was shown to be wrong, and although white fumes of the oxide are formed when the steel is heated the actual molybdenum loss is negligible.

Compositions of Molybdenum Steels

This and the fact that the most suitable molybdenum content is lower than might have been anticipated are probably responsible for the slowness with which molybdenum steels were accepted by the trade. All the SAE steels specify less than 0.30% molybdenum. Few structural or low-alloy tool steels specify over 0.65% although in some high-silicon or high-chromium steels the molybdenum may reach 1%.

The decarburization effect is now inhibited by specifying a silicon content higher than in ordinary carbon steels or by protecting the surface during heating either by a controlled atmosphere or by a coating of borax.
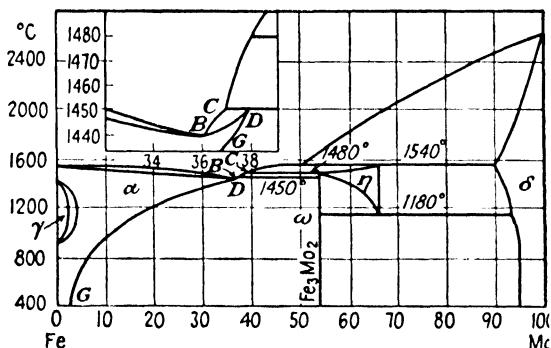
FIGURE 21.3. The iron-molybdenum equilibrium diagram (from *National Metals Handbook*).

The Iron-Molybdenum Equilibrium Diagram

The iron-molybdenum equilibrium diagram (Figure 21.3) is strikingly similar (especially in the low-alloy region) to the iron-tungsten diagram (Figure 22.1). The reader is referred to the *National Metals Handbook* for a complete description of the various phases indicated

in both diagrams. A noteworthy fact is that the alpha phase boundary that encloses the gamma loop in the iron-molybdenum diagram indicates that the gamma phase is completely eliminated above 3% molybdenum. In the iron-tungsten system this occurs at about 6% tungsten. The difference in solid solubility in the gamma phase might be taken as indicative of the relative effects of the two alloys in altering the physical properties, with the element of lower solubility showing the greater effect. Similar relationships are well known in the brasses, bronzes, and aluminum alloys.

Replacement Numbers

It may be taken as a general rule that where the equilibrium relationships between a parent metal and several solute alloying elements are similar, the maximum effect of the solute in altering the properties of the parent metal occurs at saturation values of the solute. The maximum effects are frequently quite similar and hence, if the alloying elements be arranged in the order of their saturation values, this will also be the order of amount required to produce a given effect. The number representing the position of an element in such a series is sometimes called its replacement value. Thus several times as much chromium (which forms a gamma loop with a maximum at about 15%) is required and permissible in most of the structural chromium steels, as either molybdenum or tungsten.

As with chromium, the effect of carbon is greatly to expand the gamma loop for both molybdenum and tungsten.

The solubilities in the alpha phase of the intermetallic compounds of iron and molybdenum and of iron and tungsten are shown to decrease rapidly with temperature. This circumstance greatly complicates the structural relationships in the high-alloy compositions such as the high-speed steels and results in the formation of complex and unpredictable carbides offering possibilities for numerous useful qualities in the steel and requiring unusual heat treatments.

S Curves for Molybdenum Steels

The S curves for the low-molybdenum structural steels are very illuminating, and it is to them that much of the progress in the use of molybdenum steels is due. The shelf, or bay, in the Ar' region has been noted before (Chapter XIX). It is found also in S curves for the chromium steels. The effect of molybdenum and chromium together seems to accentuate this bay greatly. A typical and popular example is the S curve for SAE 4140 steel (Figure 21.4). The effect of the molybdenum seems greatest in moving the upper part of the curve

to the right; that is, it increases the time required to form pearlite.

Figure 21.5 is an S curve for a carbon-molybdenum steel. The effect of the molybdenum in the upper part of the curve is quite evident, but it is also evident that in the bainite region below the shelf the molybdenum has had but slight effect. This is characteristic of molybdenum and explains many of its advantages. High quenching speeds
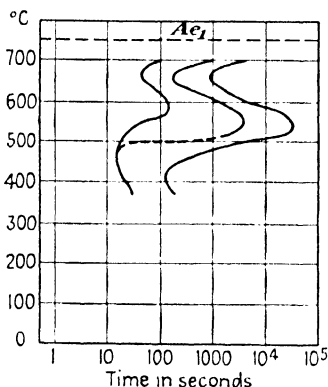
FIGURE 21.4. *Subcritical transformation curve for SAE 4140 steel* (redrawn with modifications from *Molybdenum in Steel*, Climax Molybdenum Company, Section 1, page 10).
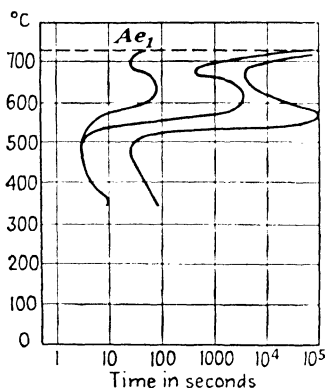
FIGURE 21.5. Subcritical transformation curve for steel with composition 0.42% C, 0.71% Mo (redrawn with modifications from *Molybdenum in Steel*, Climax Molybdenum Company, Section 1, page 9).

are not required to allow such steels to transform in the bainite region, and thus structures and physical properties are produced that are not attained easily in most other steels. By selecting a suitable quenching rate, part of the steel may be changed to bainite and part will transform to martensite, which will respond to later tempering. Stresses are less in the martensite formed under these conditions, and a sounder heat-treated steel results.

Hardenability of Molybdenum Steels

The effect on depth of hardening of the delayed transformation, as shown in the higher temperature levels by the S curve, should be apparent. Bainite structures of high strength and toughness should be produced at great depths by ordinary quenching. Actually, molybdenum steels are recommended for hardenability. However, if full hardening is required (that is, if it is desired that the steel quench to martensite in the deeper regions) other alloys that tend to delay the transformation at the lower temperature levels should be added. For

this reason chrome-molybdenum steels, such as SAE 4140, or chrome-nickel-molybdenum steels, such as SAE 4340, are highly popular. A few typical analyses of molybdenum steels are given in Table 1.

TABLE 1. Typical Molybdenum Steels

Type of alloy	Specification number	Typical or average analysis (%)					
		C	Mn	Cr	Ni	Si	Mo
C-Mo.........	....	0.36	0.69			0.24	0.22
Cr-Mo........	SAE 4120	0.20	0.70	0.70		0.25	0.25
Cr-Mo........	SAE 4130	0.30	0.50	0.95		0.20	0.20
Cr-Mo........	SAE 4140	0.38	0.67	0.95		0.20	0.20
Cr-Ni-Mo......	SAE 4320	0.20	0.55	0.45	1.80	0.25	0.25
Cr-Ni-Mo......	SAE 4340	0.40	0.65	0.65	1.75	0.20	0.35
Cr-Ni-Mo......	NE *8630	0.30	0.80	0.50	0.55	0.25	0.20
Cr-Ni-Mo......	NE 8650	0.50	0.90	0.50	0.55	0.25	0.20
Mn-Si-Cr-Ni-Mo	NE 9440	0.40	1.05	0.45	0.45	0.30	0.12

* National Emergency steels developed during World War II.

Other Effects of Molybdenum

Three other effects of molybdenum are: (1) its effect on creep, (2) its effect on temper brittleness, (3) its effect on the impact value.

Creep

This quality is defined as the tendency of a metal to flow or stretch slowly at elevated temperatures under an applied load that is lower than the elastic limit. Creep is evaluated in terms of elongation in inches per inch in 1000 hours at temperature $t°F$. Much study has been spent on the causes and remedies for high creep values, but molybdenum is known definitely to increase resistance to creep in steels and to raise the strength of steel at elevated temperature.

Temper Brittleness

Temper brittleness appears in some steels when they are cooled slowly from their tempering temperature (750° to 1000°F). It is manifested by a low impact value. It is capricious in nature and due to obscure causes; with similar analyses some steels will show it and others will not. It seems quite definitely established, however, that temper brittleness is the result of precipitation hardening consequent upon the formation of submicroscopic crystals of compounds of some of the minor constituents with the steel. These minor constituents may

be oxides, nitrides, or intermetallic compounds such as are thought to form with some of the alloying elements. These compounds are assumed to be soluble in ferrite at temperatures near the critical range but practically insoluble at room temperature.

Chapter XXVII on aluminum discusses the mechanism of precipitation or age hardening. Molybdenum is perhaps the most effective element in inhibiting temper brittleness and in the quantities ordinarily used in molybdenum steels it practically eliminates the difficulty. The mechanism of this effect is still obscure.

Impact Value

Molybdenum appears to raise the impact value of steel. However, it is not perfectly clear that this is more than the accompaniment to the increased strength and physical properties that result from the other effects of molybdenum.

Reasons for Behavior of Molybdenum Steels

In consideration of the many remarkable effects of quite small concentrations of molybdenum in steel, it seems unlikely that their explanation can be found in the mechanical properties of the molybdenum itself or even in its carbides. Like tungsten, it forms very hard carbides and in the high-speed steels these carbides display their own physical characteristics, but in the low-alloy steels the major portion of the carbide is Fe_3C. It is to the structure of the steel and the distribution of the carbides that we must look then for the explanation of the physical properties.

The S curves (Figures 21.3 and 21.4) indicate that it is easy to secure a fine distribution of the carbides, either as bainite or as tempered martensite. Once formed, these carbides do not grow readily as in carbon steels, and high tempering temperatures are necessary to secure the same degree of softening as would be obtained at much lower temperatures in carbon steels. This is in keeping with the high hardenability and low creep values.

QUESTIONS

1. What is the percentage of carbon in Cr_7C? in Cr_4C?
2. What other alloying elements form gamma loops with iron?
3. What is the effect of chromium upon the eutectoid temperature and upon the eutectoid composition?
4. What is the effect of chromium on the delta-gamma transformation?
5. Why should an increased temperature of heating above Ac_3 be especially effective in increasing hardenability of chromium steels?

6. How much chromium would form Cr_4C in a stainless steel containing 0.04% carbon if all the carbon combined with the chromium?

7. Why should not a cutlery-type stainless steel be heated much above 1800°F to effect solution of carbides?

8. What is the function of the nickel in 18–8 stainless steel?

9. Why is heat-treated stainless steel not very "stainless" if heat treated to improve physical properties?

10. What use is made of molybdenum in analytical chemistry?

11. Should the effect of molybdenum in raising the Ac_1 temperature account for its effect on hardenability?

12. If molybdenum is given the value 1, what are the replacement values of tungsten and chromium respectively?

13. A popular explanation for temper brittleness is that it is due to an obscure precipitate phase that forms upon slow cooling from the tempering temperature. How can the effect of molybdenum be made to fit this idea?

Specific Characteristics of Tungsten Steels and of Tungsten and Molybdenum High-Speed Steels

Limited Use of Low-Alloy Tungsten Steels · Development of Tungsten High-Speed Steel · Composition, Manufacture, and Uses · Heat Treatment · Iron-Tungsten Equilibrium · Replacement Values in High-Speed Steel · Theory of the Heat Treatment · Secondary Hardness · Final Microstructure · Effects of Other Elements · Molybdenum High-Speed Steels · Compositions and Heat Treatment

Limited Use of Low-Alloy Tungsten Steels

It is said that tungsten in amounts less than 1% does not pay its way in steel. Although this is perhaps too broad a statement when all purposes are considered, it is, nevertheless, difficult to see how tungsten in competition with cheaper chromium and molybdenum can be justified in low-alloy constructional steels. A few steels containing from 1% to 3.50% tungsten are popular for fast finishing tools and wire drawing dies. They range from 1.25 to 2% carbon. The tungsten seems to confer a peculiar tough hardness which, in machine tools, permits very smooth finishing cuts at high speed. They cannot, however, operate at speeds that heat the tip of the tool to a red heat as do the high-speed steels.

Development of Tungsten High-Speed Steel

The most important tungsten steels are the high-speed tool steels. These date from experiments performed in 1900 by Taylor and White who were then in the employ of the Bethlehem Steel Company. By

1915, improvements in composition and heat treatment had produced alloys of iron with tungsten that were essentially the same as those in use today.

Later developments consisted of a better understanding of the reasons for the behavior of high-speed steel with attendant improvements in heat treatment, improvements which, though minor in character, are important from the standpoint of minimizing danger of cracking and securing optimum performance. The successful substitution of molybdenum to produce the now popular molybdenum high-speed steel was not effected until 1932.

Composition, Manufacture, and Uses

The standard and most popular tungsten high-speed steel, known as the *eighteen-four-one* composition, has the average analysis: 0.70% C, 18.00% W, 4.00% Cr, 1.00% V. Variations from this analysis include the addition of molybdenum and cobalt, and limited changes in the percentages of chromium, vanadium, and tungsten.

Such high-speed steel is cast into ingot form and rolled or forged into final stock size. The reduction by rolling or forging should be great in order to break up coarse carbide structures which cannot be destroyed by heat treatment alone. (See Figure 22.3.)

The uses of high-speed steel are as varied as those of any tool steel and include the manufacture of such articles as lathe tools, drills, punches, dies, milling cutters, hack saws, and band saws. Correctly heat treated, their cutting speed is several times that of carbon steel tools, and they retain their hardness and cutting ability even when the cutting tip or edge reaches a visible red heat.

Heat Treatment

The standard heat treatment for high-speed steel tools is as follows:

1. Heat slowly to 1450° to 1600°F. If large sizes are being treated by charging into a hot furnace it is advisable to use two furnaces, one heated to 1100° to 1200°F, and one to 1450° to 1600°F. After reaching the temperature of the first furnace the pieces are transferred to the second. Slow heating through the critical range is necessary to avoid cracking.

2. After reaching the temperature of the second furnace, or 1450° to 1600°F, the pieces are transferred to a high temperature furnace where they are brought as rapidly as possible to a temperature of 2350° to 2400°F. They should be held at this temperature only long enough to become heated throughout. The rapid heating is to avoid excessive scaling. The high temperature, which is just below that at

which the pieces would start to melt (temperature of incipient fusion), is for the purpose of effecting the maximum possible solution of carbides in the shortest possible time.

3. The pieces are removed from the furnace and cooled at a moderate to rapid speed. Air cooling is often sufficient. An oil quench is usually permissible. Hot water can be used but not cold water. A common practice consists in halting the quench at 250° to 300°F and tempering immediately from that temperature. A molten bath held at 1100°F may be used for the quench after which the pieces may be air cooled to 250° to 300°F.

4. Tempering, or rather secondary hardening, consists in reheating to 1025° to 1150°F for fifteen minutes or more. This hardness is not reduced and may even be intensified by subsequent heating to the same temperature.

Iron-Tungsten Equilibrium

To explain the treatment and behavior of high-speed steel we may first consult the iron-tungsten equilibrium diagram (Figure 22.1). By
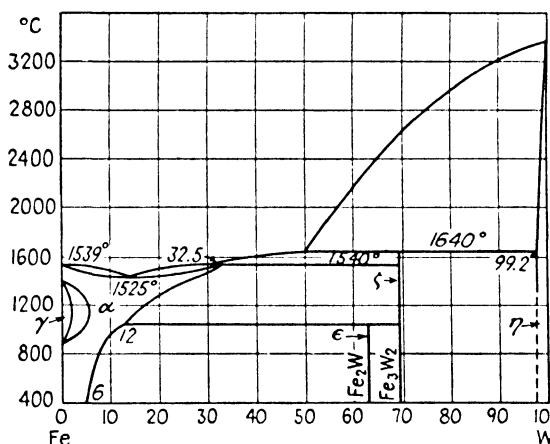
FIGURE 22.1. The iron-tungsten equilibrium diagram. (Redrawn from *National Metals Handbook,* 1939).

itself, this diagram offers limited assistance. However, we note that the alpha phase boundary enclosing the gamma loop shows the gamma phase to be eliminated in alloys containing more than 6% tungsten. We note also the peritectoid reaction by which, upon cooling, the alpha phase and zeta phase (Fe_3W_2) combine to form the epsilon phase (Fe_2W) at 1904°F. Finally, we note how rapidly the boundary

of the alpha phase in equilibrium with Fe_2W slopes to the left, indicating comparatively low solubility of tungsten in iron at room temperature.

To analyze fully the phase relationships in high-speed steel it will be necessary to attempt some understanding of the ternary iron-carbon-tungsten system. Although a complete equilibrium diagram is not available for this system it seems well established that a ternary compound,
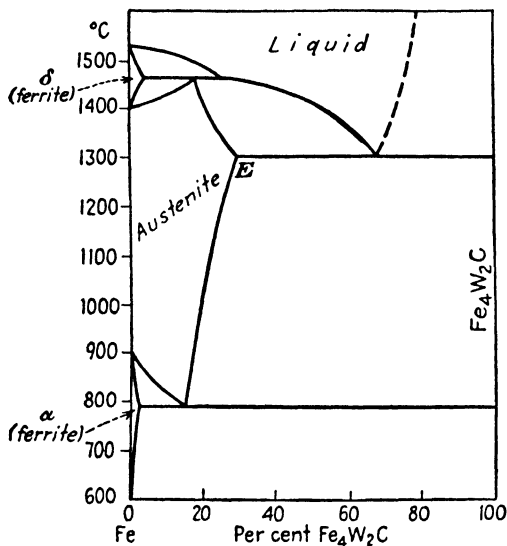
FIGURE 22.2. The pseudo-binary constitution diagram of Fe-Fe_4W_2C (redrawn by permission from *High Speed Steel*, by M. A. Grossmann and E. C. Bain, published by John Wiley and Sons, Inc., 1931).

Fe_4W_2C, exists, and this compound has fairly consistent binary equilibrium relationships with austenite and ferrite. Grossmann and Bain in their book *High Speed Steel* present the pseudo-binary [1] diagram shown in Figure 22.2.

The compound Fe_4W_2C requires approximately 61% tungsten and 2% carbon. The diagram shows point E at 30% of the compound. This corresponds to 18% tungsten and 0.60% carbon in the alloy, almost the specified composition for high-speed steel. This means that theoretically, at least, all the tungsten and most of the carbon should be dissolved in the austenite at the temperature of point E. Actually, this does not happen, partly because of the sluggishness with which the double carbide dissolves, but also because in high-speed steel the other

[1] This is not a true binary alloy system since it develops compositions not in the plane of the diagram.

carbide-forming elements (chromium and vanadium) can replace or be substituted for the tungsten in the double carbide formula. Thus 1% of the chromium from the analysis given above can account for the 0.10% carbon that was not included in the Fe_4W_2C, leaving 3% chromium to alter the properties of the austenite at high temperatures, or the ferrite at low temperatures.

Replacement Values in High-Speed Steel

In evaluating the effects of the different carbide-forming elements, the idea of replacement values, mentioned under molybdenum steels, is useful. As can be seen from the equilibrium diagrams, these values are approximately proportional to the maximum solubilities of the elements in gamma iron. Thus 1% tungsten is equivalent to, and may be replaced by either 2% chromium, $\frac{1}{6}$% vanadium, or $\frac{4}{7}$% molybdenum.

The presence of undissolved carbides throughout the temperature range of solid high-speed steel is beneficial and definitely improves cutting ability. However, in heat treatment the more carbide taken into solid solution at the high heating temperature the better the hardening properties and performance.

Theory of the Heat Treatment

The reasons for the elaborate heat treatment of high-speed steel now become apparent. From the pseudo-binary diagram, Figure 22.1, it is seen that the 18–4–1 composition will result in austenite dendrites surrounded by the austenite-carbide eutectic. This eutectic is of the picturesque or graphic type so often found in complex alloys (Figure 22.3), and in it the carbide portion forms a more or less continuous network between the dendrites. Since this carbide cannot be entirely dissolved in the austenite at any temperature, it must be broken up into discrete particles by rolling or forging after the steel has been initially cast into ingot form.

The high quenching temperature, 2400°F, corresponds to point E on the diagram (Figure 22.2) and results in solution of the maximum amount of carbide. Sluggishness, induced by the uncombined chromium or tungsten, inhibits the eutectoid transformation as well as the pro-eutectoid carbide precipitation at moderate cooling rates. Transformation to martensite commences at some temperature below 500°F but is not complete if the temperature is not carried below about 250°F. This allows soft, untransformed austenite to assimilate transformation strains which might crack the fully hardened piece at lower temperatures.
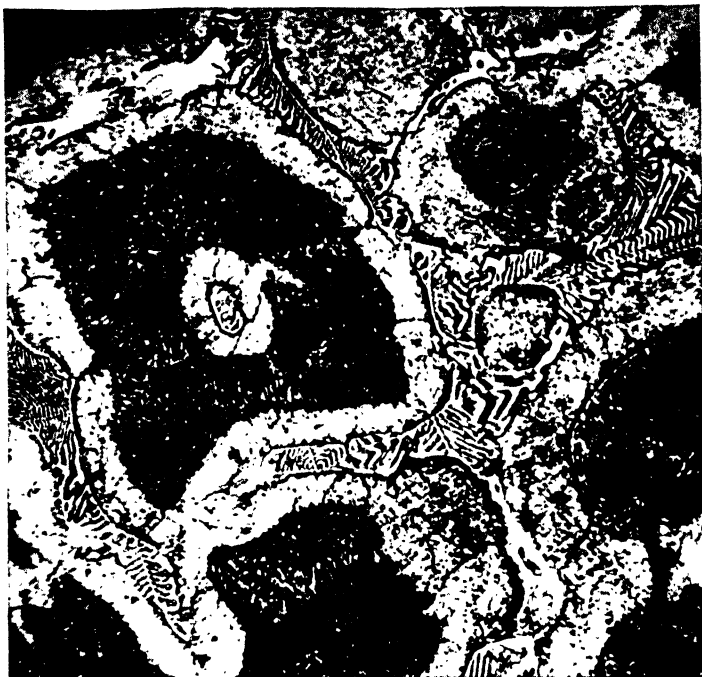
FIGURE 22.3.   Cast high-speed steel, 500×.

Secondary Hardness

Finally, the reheating to 1100°F results in almost, but not quite complete, precipitation of carbides from the residual austenite and a slight tempering of the martensite. In any case, the carbide formed by this last treatment is submicroscopically fine and produces a structure that has greater hardness than the quenched material. This is called *secondary hardness.*

Final Microstructure

The final structure consists of the undissolved carbide fragments embedded in a matrix that varies in appearance from that of a slightly tempered martensite to a black, unresolvable troostite (fine sorbite) as shown in Figure 22.4. Grain boundary lines are probably pseudomorphs of austenite grain boundaries, where the transformation and carbide precipitation has progressed farther than at other places.

Effects of Other Elements

Vanadium, for some unexplained reason, increases the cutting ability of high-speed steel tools. Its effect on grain size in the austenite is not

so marked as in the lower-alloy steels and apparently of little significance.

From 1 to 5% cobalt is frequently added to high-speed steel which is to be used to cut hard or gritty materials such as sand castings. The effect of the cobalt is probably to stiffen the iron matrix. It possi-
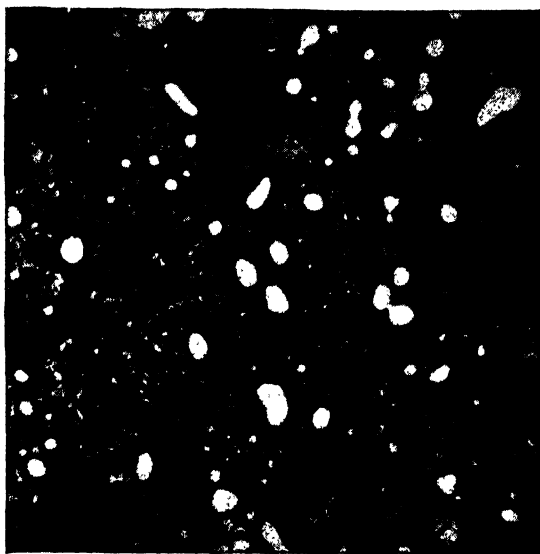
FIGURE 22.4. Heat-treated high-speed steel, 2000×.

bly increases the tendency toward carbide precipitation on tempering, as might be gathered from the S curve for cobalt steel (Figure 19.10). It will be remembered that cobalt, unlike most elements, increases the rate of transformation in the *Ar′* region.

Cobalt high-speed steels require slower cooling from the forging temperature and, in general, require more careful treatment than other types.   .

Molybdenum High-Speed Steels

Since 1932 the substitution of molybdenum for tungsten in high-speed steel has been increasingly successful. The difficulties that discouraged earlier development, namely, the tendency to decarburize and softness in the surface metal, have been overcome by such devices as controlled furnace atmospheres, salt bath heating, and in some cases coating the surface of the pieces with borax.

Compositions and Heat Treatment

Three principal compositions are:

Component	Composition, per cent		
	Type I	Type II	Type III
Carbon.............................	0.70–0.85	0.70–0.90	0.75–0.90
Tungsten...........................	1.25–2.00		5.00–6.00
Chromium..........................	3.00–5.00	3.00–5.00	3.50–5.00
Vanadium..........................	0.90–1.50	1.50–2.25	1.25–1.75
Molybdenum........................	8.00–9.50	7.50–9.50	3.50–5.50

Cobalt up to 9% may be used in all three types.
Type II eliminates tungsten by increasing the vanadium.
Type III is a combination tungsten molybdenum alloy that avoids most of the decarburizing effects of the higher molybdenum types.

The molybdenum high-speed steels require somewhat more care in heat treatment than the tungsten high-speed steels. Annealing prior to hardening or rehardening is practically imperative. The hardening temperature is slightly lower (maximum 2250°F compared with 2400°F for the tungsten steels). Quenching is best done in a salt bath maintained at 1100°F from which the articles should be cooled in air to room temperature and tempered immediately. The tempering temperatures are the same as for tungsten high-speed steels. These operations are not difficult or costly even in a small plant so that now molybdenum high-speed steels are acquiring popularity equal to that of steel with tungsten.

Yet there can be no doubt that tungsten is a very desirable element even in the molybdenum high-speed steels. In some respects the type III steel listed in the table is the most usable and of the three requires the least modification of heat treatment. It seems likely, therefore, that future developments may tend toward combinations of tungsten and molybdenum in which costs, quality, and utility will be adjusted to suit all practical needs.

QUESTIONS

1. Appraise tungsten as an alloying element in regard to carbide-forming tendencies; space lattice; solubility in the alpha and gamma phases; effect on the critical temperature; and effect on rate of transformation.

2. Is the high solution temperature in the heat treatment of high-speed steel merely for the purpose of saving time?

3. Is the eutectic structure in a complex alloy like high-speed steel necessarily a true eutectic? Under what conditions does it form?

4. Can you explain all the features of structure in the cast high-speed steel? (See *High Speed Steel,* by Grossmann and Bain.)

5. Cobalt and nickel are considered similar chemically. Is there any similarity in their behavior as alloys in steel?

6. What is there about the chemistry of molybdenum oxide and of borax that might explain the protective effect of borax?

7. High-speed steels quenched to about 150°C and immediately reheated do not acquire as great hardness as those quenched cold, but there is more danger of cracking in the latter. Can you think of a still better treatment?

8. Why is nickel objectionable in high-speed steel and in tool steel?

CHAPTER XXIII

Copper: Manufacture and Properties

Occurrence and Ores of Copper · The Economics of Copper Production · Copper Smelting · Commercial Grades of Copper · Uses of Copper · Physical Properties of Copper · Chemical Characteristics of Copper · Impurities in Copper

Probably the first metal used by mankind for purposes other than ornament was copper, and while it has been superseded by steel in many of its original uses such as weapons, tools, and structural parts, it stands alone in its usefulness as a conductor of electricity. Second only to iron in quantity produced, it is excelled in this valuable characteristic by only silver whose rarity and cost rule out that metal as a common commercial substitute for copper.[1] Aluminum is the only competitor, and cost plus difficulties in welding and fabrication put aluminum definitely in second place.

Occurrence and Ores of Copper

The metallurgy of copper is complicated by the fact that it occurs in a variety of different kinds of ores. It is in combination with different substances in different ores, and its different combinations require different treatments. Also, it is frequently associated with noble metals, notably gold and silver. These need to be isolated and recovered. Nickel is sometimes found with copper and presents an especially difficult problem in its separation. In the case of one ore containing

[1] During World War II silver was loaned by the government for use in electrical equipment in some war production plants. This silver, being totally recoverable and returnable, served to circumvent critical shortages in copper.

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both nickel and copper, the relative amounts of the two substances are in proportions that form a useful alloy, namely, Monel metal (65% Ni-35% Cu). Under these circumstances they often are not separated but are smelted together.

Copper occurs in various combinations with sulphur, some of which also contain iron. Other combinations are oxides, carbonates, a silicate (chrysocolla), sulphates, the oxychloride [$Cu_2Cl(OH)_3$], sulpharsenide (Cu_3AsS_4), and sulphantimonide ($Pb_2Cu_2Sb_2S_6$). Copper also occurs uncombined as native copper. While most of these forms are used as ores, by far the largest amount of copper is produced from the sulphide ores. Table 1 summarizes the principal copper minerals.

TABLE 1.   Mineralogical Occurrence of Copper

Classification	Mineral	Formula
Carbonates	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Native copper	Copper	Cu
Oxides	Cuprite	Cu_2O
	Melaconite	CuO
Oxychloride	Atacamite	$CuOHCl \cdot Cu(OH)_2$
Silicate	Chrysocolla	$CuSiO_3 \cdot 2H_2O$
Sulphantimonide	Tetrahedrite	$4Cu_2S \cdot Sb_2S_3$
Sulpharsenide	Enargite	$3Cu_2S \cdot As_2S_5$
Sulphates	Brochantite	$CuSO_4 \cdot 3Cu(OH)_2$
	Chalcanthite	$CuSO_4 \cdot 5H_2O$
Sulphides	Bornite	$2Cu_2S \cdot Fe_2S_3$
	Chalcocite	Cu_2S
	Chalcopyrite	$Cu_2SFe_2S_3$
	Covellite	CuS

The Economics of Copper Production

This is much more involved and complicated than that of iron production. The national and world production of copper varies greatly. In the United States during 1922, a total of 511,970 tons was produced. By 1929 this increased to 1,026,348 tons, but dropped to 524,631 tons in 1931. In 1933 only 233,649 tons were produced; in 1940 about 823,-000 tons. During these intervals the price changed from a minimum of 12.75¢ per pound in 1920, to a maximum of 23.87¢ in 1929, and down to 6.125¢, minimum in 1931. In 1940 the price was 11.25¢. The cost of smelting and refining of the different ores of copper varies tre-

mendously so that it will be realized that the price will determine the ores of copper to be smelted. Each cent increase will cause operation of mines and smelters that would be shut down at lower price levels. As soon as these commence operating, however, the increased production lowers the price again. Many copper mine stock promotion schemes are founded on property that can be operated only under fair weather price conditions. There is a great deal of copper in the world but most of this supply cannot be mined profitably at normal price levels.

Copper Smelting

The different types of copper ore naturally require different smelting processes. It is not within the scope of this book to discuss all these processes or their details. However, the sulphide ores are the most common and, because it illustrates many of the chemical and metallurgical principles involved in copper smelting generally, the smelting of the sulphide ores will be outlined and briefly discussed.

Chemistry of Smelting the Sulphide Ores

The chemistry upon which the sulphide smelting is based involves first the relative stability at high temperatures under reducing conditions of cuprous sulphide (Cu_2S) and ferrous sulphide (FeS). Under such conditions these are formed from higher sulphides and melt together to form the semi-metallic mixture known as matte. The rest of the ore in the form of slag separates from the matte. The slag is formed by suitably fluxing the rock or "gangue" which composes the valueless part of the ore. The matte carries with it gold, silver, and other metals or metallic sulphides which can be isolated and recovered later in the process.

Oxidation of the matte changes the iron-copper sulphide to iron oxide and leaves the copper as sulphide. The iron oxide enters the slag and is removed. The SO_2 volatilizes. Later the unique reaction

$$2Cu_2O + Cu_2S \rightleftharpoons SO_2 + 6Cu$$
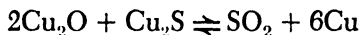
is used in isolating the copper.[2] The metallic phase now consists of an impure and somewhat over-oxidized copper together with any gold, silver, or other noble metals that may have been present in the ore. This is known as *blister copper*, and corresponds roughly to the pig iron stage of steel manufacture. It is much purer than pig iron how-

[2] This does not work with nickel, and in smelting mixed sulphide ores of copper and nickel to produce Monel metal, other methods are employed to bring the nickel into the metallic phase.

ever. Final purification is accomplished by furnace refining followed by electrolysis.

The Process of Smelting and Refining

Briefly, the smelting process is as follows: Starting with the ore after any mechanical concentration (ore dressing) methods have been applied, the first step consists in a preliminary roasting (heating in air) to remove some of the excess sulphur. This is followed by heating in a reverberatory or blast furnace to produce the molten matte. The reverberatory furnace is similar to an open hearth but is not regenerative and operates at a lower temperature.

The mattes from both blast furnace and reverberatory furnace are transferred to the copper converter. Air is blown through the molten matte, oxidizing the sulphur and iron and producing the impure blister copper.

Preliminary refining is accomplished after the converter treatment in another reverberatory furnace by first continuing the oxidation and removing the slag until all sulphur and impurities, such as arsenic and antimony, are oxidized. This oxidizing treatment is known as "flapping." Then the reaction is reversed, and by stirring with poles of green wood the dissolved copper oxide is reduced to metallic copper. The copper is then cast into slabs suitable for electrolytic refining.

The copper slabs contain any gold or silver that may have been present in the ore. These may be separated by making the copper the anode in an electrolyzing bath (consisting chiefly of copper sulphate and sulphuric acid). The copper is carried to the cathode by means of the electric current. All impurities, including gold and silver, collect as an anode slime which is treated for the recovery of these metals.

```
                    MINE
                   /  |
                  /   |
   Ore concentrator   |
                  \   |
                   \  ↓
                   Roaster
                  /        \
 Reverberatory(Matte)     Blast furnace(Matte)
                  \        /
                 Converter  (Blister copper)
                      ↓
              Refining furnace (Anodes)
                      ↓
              Electrolysis (Cathodes)
                      ↓
         Melting furnace(Tough-pitch copper ingots)
                      ↓
                   Market
```

FIGURE 23.1.   Basic outline of copper smelting.

The electrolyzed copper is extremely pure but not in the best condition for electrical use. It is sometimes remelted in another reverberatory furnace and brought to the proper condition of deoxidation by poling with green wood poles.

Poling Procedure

The poling procedure requires considerable skill since it determines the soundness of the copper ingots and freedom from defects, such as pipe and blowholes. Also, the oxide content is lowered to the point where the copper is not embrittled by the Cu_2O-Cu eutectic which occurs at 0.35% oxygen. The extent of poling is determined by the appearance of the top of a small test ingot. If, upon freezing, the top is sunken, it indicates the presence of oxide and the copper is insufficiently poled. If the top is bowed up it is overpoled. This is due to the presence of gases, probably hydrogen, nitrogen, and water vapor, which dissolve in the copper when the oxygen content is low.

Underpoled copper breaks up in rolling and has a brick red fracture due, in part, to the oxide particles. Overpoled copper is spongy, of low density, and unfit for casting purposes. In correctly poled copper, the test ingot shows a flat top. Some deep-seated, small gas pockets (blowholes) are present, but these serve to overcome the shrinkage and piping tendency and to indicate that nearly all the oxide is reduced.

If the poling is carried too far it is difficult to correct the situation. The gases that are absorbed as a result of the lowered oxygen content, particularly hydrogen, are held tenaciously by the copper and are not removed until the copper is again saturated with oxygen. This means that the bath must be over-oxidized again by flapping or adding copper oxide and the entire poling operation repeated.

Commercial Grades of Copper

Copper that is correctly poled as indicated by the set or pitch of the test ingot is called *tough-pitch* copper.

Other forms in which copper is available commercially are: oxygen-free copper, deoxidized copper, electrolytic cathodes, and Lake copper. *Oxygen-free copper* is made by casting pure copper under conditions that prevent oxygen absorption. Several methods are used including a form of die casting and extrusion of cathode copper heated to near its melting temperature. *Deoxidized copper* is made from tough-pitch copper by adding a strong reducing agent, such as phosphorus or silicon (sodium and lithium also have been experimentally tried) to the molten metal. It shrinks deeply when cast. *Electrolytic cathode copper* refers to the unremelted cathodes. They are used in this form for making alloys, for example, brasses and bronzes. *Lake copper* is non-electrolyzed copper from the Lake Superior district. It is sufficiently pure without electrolytic refining and is cast directly into tough-pitch copper. It *may* contain small amounts of silver or arsenic.

Uses of Copper

Over 50% of the copper produced is used for electrical purposes, most of this being in the form of wire, switches, bus bars, and articles that must carry electric current. For these purposes tough-pitch copper of high conductivity is used. Of the remainder, articles requiring high heat conductivity account for a large portion. A large tonnage goes into automobile radiators, and somewhat less into hot water heaters for household use.

Other uses take about 25% of the production and include roofing, tubing, and alloys. The alloys constitute the greatest portion of this allotment, the principal alloy being that with zinc, namely brass. For the manufacture of alloys, cathode copper is usually used since the advantage of deoxidation by poling would be lost in making the alloy.

For articles requiring higher strength than is obtainable with tough-pitch copper, copper containing small amounts (less than 1%) of various elements, e.g., arsenic, antimony, cadmium, bismuth, phosphorus, silver, is used. Arsenical copper is the usual type. In such coppers, however, the electrical conductivity is considerably reduced. These low-percentage constituents are usually impurities that occur naturally, although arsenic is sometimes added.

Physical Properties of Copper

Electrical Conductivity

The most important physical properties of copper are its electrical properties, and of these the conductivity is the most often utilized. The conductivity is usually expressed as a per cent of a standard value that was established in 1913 and which represented the average value for the best commercial copper produced at that time. It was called the *International Annealed Copper Standard* (IACS). This standard designated a wire 1 meter long and of 1 square millimeter cross section as having a conductivity of 58 mhos at 20°C.[3] Actually, copper may have a conductivity equal to more than 102.3% IACS. Lake copper may have a conductivity as low as 99.3% IACS. This variation in values for different grades of what is apparently high purity copper illustrates the fact that extremely small quantities of impurities exert a large effect on this important property. Arsenical copper with 1% of arsenic may have a conductivity about one-half that of the best electrical copper.

[3] This corresponds to a resistance of 1.7241 microhms across a centimeter cube or a resistance of 0.15328 ohm in a wire weighing 1 gram and measuring a meter long. It assumes an average density of copper equal to 8.89 grams per cubic centimeter.

Thermal Conductivity

This is closely related to electrical conductivity. A value of 0.923 calorie per sec per sq cm per cm per degree centigrade is average although very pure copper would have a value about 2% higher. Single crystals of copper have a considerably higher value (0.989 calorie). A variation in thermal conductivity has a corresponding variation in electrical conductivity so that the ratio

$$\frac{\text{thermal conductivity}}{\text{electrical conductivity} \times \text{absolute temperature}} = \text{constant}$$

is approximately true.

Thermoelectric Properties

Copper is used for its thermoelectric properties in the case of copper-constantan thermocouples for temperature measurement. Constantan is a copper-nickel alloy containing about 60% copper. Pure copper has about the same thermoelectric effect as pure iron. This is odd when we consider how different the two metals are in other ways. When a couple is made of copper and iron there is a small emf with the copper element positive up to about 300°C, above which temperature the iron is the positive element. At one point near 300°C the emf is zero. However, either copper or iron gives a high emf when coupled with constantan.

The magnetic properties of copper are of theoretical interest only, and apparently dependent largely on minute traces of the iron that is unavoidably present in commercial copper.

Density

Since conductivity is usually based on volume or cross-sectional area, the density of copper has some importance. This may vary from 8.4 grams per cubic centimeter in cast tough-pitch copper (at 20°C) to as high as 8.92 grams for some forms of rolled copper and oxygen-free copper. One authority gives a value of 8.953 grams for a single crystal. Apparently, copper of maximum density is difficult to produce.

Tensile Properties

The tensile properties vary greatly with minute variations in composition and with degree of cold working and heat treatment. A low value of 31,584 psi is recorded for annealed bars containing 0.015% oxygen.[4] The same material cold rolled stood 48,384 psi.

[4] *Copper and Copper Base Alloys,* by Wilkins and Bunn, McGraw-Hill Book Co., 1943.

TABLE 2.   Some Tensile Values for Various Kinds of Copper

Designation	Form	% Cu	U.t.s., psi	Y.P., psi	Elong., %	Authority
Electrolytic tough pitch	Rod	99.03	33,000	6,000	50	Ref. 1
Same, hard drawn. . . .	Rod	99.03	55,000	43,000	10	Ref. 1
Oxygen-free high con- ductivity (OFHC) . .	Strip	99.94	32,000	6,000	43	Ref. 1
Deoxidized (0.02% P) .	Tube	99.96	35,000		45	Ref. 1
Same, hard drawn. . . .	Tube	99.96	59,000		5	Ref. 1
Arsenical tough pitch (0.45% As).	Strip	99.50	34,000	5,000	47	Ref. 1
Same, hard drawn. . . .	Strip	99.50	55,000– 60,000	49,000	4	Ref. 1
Cast, OFHC.	Cast		22,950	14,000	45.3	Ref. 2
Hard-drawn wire (0.04″ diam.).	Wire		67,000		0.85	Ref. 3
Soft wire (0.081″ diam.)	Wire		38,500		25	Ref. 3

References:
1. *Copper and Copper Base Alloys*, by R. A. Wilkins and E. S. Bunn, McGraw-Hill Book Co., 1943.
2. "Some Properties of Oxygen-Free High Conductivity Copper (OFHC)," Claus G. Goetzel, *Trans. Am. Soc. Metals*, 27:2, 458–474 (1939).
3. *National Metals Handbook*, American Society for Metals, 1939.

The range of properties outlined in Table 2 is about all that can be expected from the mechanical or heat treatment of reasonably pure copper. None of these values is sufficiently high to produce such articles as cutting tools. Stories of tempering methods used by the ancients are in all likelihood founded on inaccurate data. Undoubtedly their "tempering" method was mechanical working or peening of the edges of their tools, and their metal, far from being pure copper, was probably a tin bronze, the result of smelting ores containing both copper and tin. Modern methods can produce harder metals of this type than could the ancients.[5]

Chemical Characteristics of Copper

Copper is quite active chemically, although in a weak way. It combines with many elements like oxygen, chlorine, sulphur, and phosphorus, but not with as much energy as elements like aluminum, zinc, or iron combine. In fact, copper is on the border between noble and base metals. It is resistant to corrosion in that corrosion will not pro-

[5] For a conclusive discussion of this matter the reader is referred to Bureau of Standards Circular 73, 1922, or to J. L. Gregg, *Arsenical and Argentiferous Copper*, Chemical Catalogue Co., 1934.

ceed far below a surface layer of oxide, or whatever composes that layer.

A discussion of copper would not be complete without reference to the colors assumed when the copper corrodes under various conditions. These colored coatings are called patinas and specimens with rare or unusual colors are highly valued. We may list a few of the more common and striking patinas.

Dull ocher. The color normally obtained after a few days in moist air.

Crimson. The oxide color on the surface of cast copper ingots resulting from intense heat.

Rose red. Also the result of heat but less brilliant than the crimson color.

Black. Produced by prolonged oxidation at high temperatures.

Silvery gray black. A highly prized patina that is found on very old Chinese bronzes.

Pale bluish green. Can now be produced in a few days on copper roofs. The new roof is sprayed with a dilute ammonium nitrate solution at a time when the weather following is likely to be damp or humid but not raining. The color is due to a basic copper carbonate. This is a slimy sort of substance when wet and forms an impervious coating on the copper that is very effective in preventing further corrosion.

Bright green. Verdigris; a basic copper acetate found frequently on brass. It is very detrimental as it continues to form indefinitely in moist air and eats into the brass. It will start in the presence of acetic acid or vinegar vapors. Metal cleaning or polishing compounds that contain ammonia are best for its removal.

Impurities in Copper

The effects of impurities in copper may be listed in three categories: first, the effects on conductivity; second, the effects on tensile properties, and third, the effects on structural characteristics, chief among which are the effects on recrystallization temperature.

Effects on Electrical Conductivity

The curves shown in Figure 23.2 [6] were compiled mostly from the work of Smart and Smith and show the effects on conductivity of a

[6] Compiled from data of J. S. Smart, Jr., and A. A. Smith, Jr., given in a series of articles on effects of impurities in copper, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.,* 147, 48 (1942); 152, 103 (1943); and *Metals Technology, Technical Publication 1807,* September, 1945.
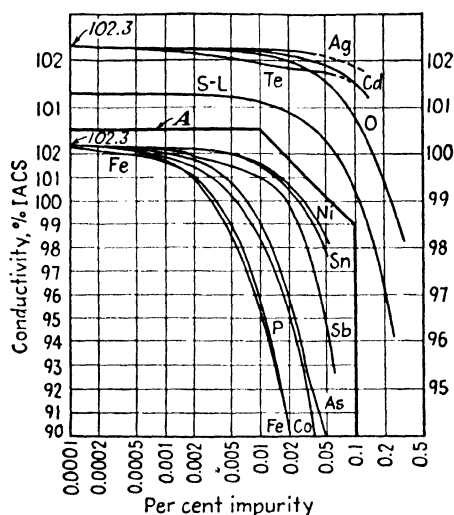
FIGURE 23.2.   Effects on conductivity of various impurities in copper. Slight adjustments introduced to give uniform zero values (data from Smart and Smith; see footnote 6, page 266).

TABLE 3.   Effect of 0.01% Impurity on Conductivity of Oxygen-Free Copper

Impurity	Conductivity % IACS	% Reduction below maximum	Authority for conductivity
None...................	102.3	0.00	1
Bismuth................		Slight	
Cadmium...............	102.25	0.07 (approx.)	1
Silver..................	102.2	0.10 (approx.)	1
Zinc...................	102.07	0.23	2
Oxygen.................	102.05	0.25	3
Tellurium........:......	101.95	0.35	1
Tin....................	101.50	0.80	1
Nickel.................	101.45	0.85	1
Antimony...............	100.80	1.50	1
Manganese..............	100.79	1.51	2
Arsenic.................	99.3	3.00 (approx.)	3
Cobalt.................	98.3	4.00	1
Phosphorus.............	95.76	6.54	2
Iron................... ..	95.20	7.10 (est.)	1

Authorities for Conductivity:
    1. Smart and Smith; see footnote 6, page 266.
    2. Smith and Palmer; see footnote 8, page 268.
    3. Estimated from curve, Figure 23.2.

number of elements that are important in copper technology. Also from these curves and other sources, Table 3 was derived. From it the relative effects of the various elements can be quickly appraised. The effects may be considered approximately linear [7] up to 0.1% in most cases but certainly not above that value. Below 0.001% all values converge, and the curves probably indicate combined, rather than specific,
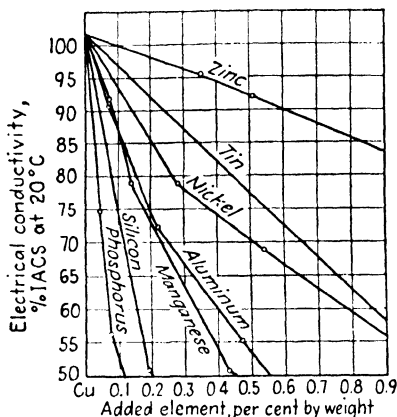
FIGURE 23.3. Effects of the impurities on conductivity of tough-pitch copper (from Smith and Palmer).

effects in the very low percentages. As is the case with most metals, methods of analysis and of purification fail when concentrations are of the order of 0.001% or lower.

The curves may be misleading if applied to commercial copper. The data were, in most cases, determined for the purest oxygen-free copper that could be produced. Ordinary tough pitch copper shows somewhat different results (Figure 23.3).[8] In some cases the data available did not quite conform to the majority of the data regarding the value for pure copper; in these instances corrections or adjustments were made arbitrarily to bring the zero values together.

As a matter of fact, there is at present no complete compendium of information regarding the effects of all elements on either electrical conductivity or other physical properties of copper. The situation is too complex to be solved easily. The results of different investigations do not show perfect agreement, and so many factors enter into the results for each composition that it is difficult to define the exact basis of classification by which any set of results can be tabulated.

Nor can the problem be dismissed with the supposition that the discrepancies are small and apply only to minute percentages of impurities, for it is in these minute percentages that the specific effects are most pronounced and subject to the greatest variation. The effect of one impurity may be affected greatly by the presence of another impurity.

[7] For the reader who is unfamiliar with logarithmic plotting, the curve marked S–L represents a linear drop of 0.2% conductivity per 0.01% impurity.

[8] "Thermal and Electrical Conductivities of Copper Alloys," by C. S. Smith and E. W. Palmer, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div., Technical Publication 648* (1935).

In general, the following may be said about impurities for which the specific effect of small quantities is great. For effect on conductivity this includes iron, phosphorus, cobalt, arsenic, manganese, antimony, and sulphur. Such elements by themselves, where no other alloying elements are present, are very detrimental to the conductivity of copper. The effect increases rapidly with increase in the amount of the impurity until the limit of solid solubility is reached. The value of the effect of greater quantities depends on the character of the precipitate phase that is formed. If it is finely divided or continuous (like a network), it usually reduces the conductivity more than if it is present in discrete particles of moderate size. In any case, the drop in conductivity will be in linear relationship to the volume of the precipitate phase rather than the per cent of alloying element that produces the precipitate phase. In the case of oxygen, the drop in conductivity is almost directly proportional to the volume per cent of Cu_2O. The solubility of oxygen in solid copper is less than 0.006% (probably less than 0.001%) and any oxygen present is in the form of Cu_2O. The specific gravity of Cu_2O is 5.88, that of copper is 8.91. From this it can be calculated that 0.01% O is equivalent to 0.1355% Cu_2O by volume. By similar calculation, 0.1% O is equivalent to 1.350% Cu_2O by volume. It can be assumed that Cu_2O has a negligible conductivity compared with copper so that these values for volume per cent of Cu_2O should roughly equal the drop in conductivity due to its presence, namely, 0.1355% and 1.350%. From the curves and table, the measured drop in conductivity due to 0.01% O is about 0.25%; that due to 0.1% O is about 1.5%. There is about the same numerical discrepancy between the two sets of measured and calculated values, although the latter set is proportionally closer. This, in itself, would suggest that copper had a slight solid solubility for oxygen, the effect of which appears in the first low concentrations and results in a constant difference between measured and calculated values for the higher concentrations. Heuer [9] explains the discrepancy on the basis of particle shape but, as stated, until more data is available on copper of high purity than is yet known the explanation must remain conjectural.

Combinations of Impurities

When more than one impurity is present their effects become more complicated. Combinations between the elements involved, with or without copper, may lower or raise solid solubilities with resulting increases or decreases in conductivity. Fortunately the usual case is a

[9] R. P. Heuer, *J. Am. Chem. Soc.*, 49, 1927 (quoted by Gregg, *op. cit.*).

lowering of solid solubility with accompanying rise in conductivity. Most of the objectionable elements combine with oxygen and one of the advantages of tough-pitch copper is that it retains enough oxygen to combine and form compounds of low solid solubility with most of the objectionable impurities such as phosphorus, iron, and antimony.

Again, some combinations produce low melting mixtures of the impurities that tend to form large spheroidized particles which affect conductivity but slightly. Reactions between impurities may take time. In the case of oxygen-bearing copper containing antimony, the formation of the oxide of antimony has been shown by Smart and Smith [10] to go almost to completion at 500°C, although the time required was over forty hours. In this time the conductivity changed from about 94% to 102% IACS.

The condition of cold working and annealing has much to do with the conductivity. The maximum value for the purest oxygen-free copper in the hard drawn state is about 100.2%. Most impurities affect the hard drawn copper to about the same extent as the annealed copper. For instance, 0.01% iron lowers the conductivity of annealed copper 7.3%, and that of hard drawn copper about 7.0%. However, nickel and tin work the other way, and oxygen-free copper containing nickel or tin has higher conductivity in the hard drawn state than in the annealed state. In the case of tin this can best be ascribed to the effect of the tin in raising the annealing temperature, and thereby rendering the anneal ineffective even up to 800°C. The formation of tin oxide, on the other hand, renders the tin ineffective and restores to the alloy the electrical properties of tough-pitch copper.

Effects of Impurities on Tensile Properties

Most of the bad effects of impurities on tensile properties are such as produce embrittlement or shortness. This would, in general, be the result of lowered ductility. *Bismuth* is the most remarkable in this respect for its effect has been noted in amounts exceeding 0.001%. Bismuth is practically insoluble in solid copper and the type of eutectic it forms around the copper crystals probably accounts for its effect. Arsenic and oxygen modify this eutectic and reduce the bad effect.

Lead, also, is highly insoluble in solid copper. Because of its low melting temperature it forms a liquid in the copper at all temperatures above its melting point of 327°C. Reference to the copper-lead equilibrium diagram (Figure 25.4) and application of the lever law

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[10] "Effect of Certain Fifth-Period Elements on Some Properties of High-Purity Copper," by J. S. Smart, Jr., and A. A. Smith, Jr., *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, **152**, 103, 107 (1943).

will demonstrate how this liquid increases in amount at higher temperatures, resulting in hot shortness. The National Metals Handbook gives 0.005% of lead as the limit above which the copper cannot be successfully hot rolled.

Cold rolling, on the other hand, is not seriously affected by the lead which is often added to copper and copper-base alloys such as brasses and bronzes to promote machinability and to improve the brasses and bronzes as bearing materials.

Iron in small amounts has little effect on the tensile properties, but between 1% and 2% iron increases somewhat the hardness and tensile strength without loss in ductility.

Arsenic and *antimony* have somewhat similar effects. Both increase the strength of copper without loss in ductility. Arsenic up to 0.5% actually improves the rolling qualities. Antimony in excess of 0.5% causes some hot shortness. Both reduce the deleterious effect of oxygen, and the hot shortness produced by antimony is eliminated by the presence of oxygen. The effect of both is to break up the fine Cu-Cu$_2$O eutectic and form coarse rounded globules of the Cu$_2$O or, in higher percentages, to form complex mixtures with the Cu$_2$O.

Silver is a common impurity in Lake or nonelectrolytic tough-pitch copper. As noted previously, its effect on conductivity is practically nil, but it has a tremendous effect in raising the recrystallization temperature.

Cadmium is the most effective element for increasing strength with minimum loss in conductivity and is added for that purpose. Copper with 0.8% Cd, according to Bureau of Standards Circular C447, may withstand 101,000 psi in cold drawn wire yet retain over 87% IACS in conductivity. Such material finds extensive use in trolley wire.

The effect of *oxygen* in small percentages, such as those which are encountered in tough-pitch copper and which may amount to 0.04% or more, is the effect of the Cu$_2$O that it forms. This would be about 0.54% Cu$_2$O. The effect of this is not great in any case, but it lowers ductility slightly if present as a finely divided eutectic. With small percentages of As or Sb this effect is practically eliminated because the Cu$_2$O becomes spheroidized in larger particles.

The deleterious effect of *sulphur* in copper has been ascribed by Hampe [11] to the formation of SO$_2$ which occurs at low temperatures by reversal of the reaction

$$SO_2 + 6Cu \rightleftharpoons Cu_2S + 2Cu_2O.$$
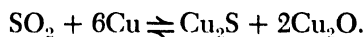
[11] Quoted in *Effect of Impurities in Copper* by S. L. Archbutt and W. E. Prytherch, Research Monograph No. 4, British Non-Ferrous Metals Research Association, 1937, page 35.

The Cu_2S is formed in the molten copper. This results in cold short-ness.

Selenium and *tellurium* probably do not behave in this way and, in general, are not as deleterious as sulphur. They are sometimes added to improve machinability.

The effect of *hydrogen* in copper is of interest and illustrates an-other principle of interaction between impurities. Hydrogen is some-what soluble in both molten and solid copper. In oxygen-free copper it apparently does no harm. However, if oxygen is present as in tough-pitch copper, the formation of water develops high internal pressures at elevated temperatures, resulting in porosity and brittleness. This is the explanation of the fact that over-poling the molten copper can only be corrected by flapping, that is, over-oxidizing that drives out the hydrogen, followed by correct poling.

Effects of Impurities on Recrystallization Temperatures

The recrystallization temperature of copper will be defined and discussed more fully in a later chapter, but the effect of impurities on that important characteristic deserves mention at this time. For practical purposes, the recrystallization temperature is nearly synony-mous with the softening temperature of cold-worked copper and cop-per alloys. It is the temperature at which the effect of work hardening begins to disappear. This was mentioned in Chapter XIV in the dis-cussion of the slip interference theory.

In general, it can be said that most elements raise the recrystalliza-tion temperature. This is to be expected and is in accordance with the stiffening effects of alloying elements in solid solutions which, as in the case of steel, result in more sluggish changes; and also with the obstructing effects of precipitate phases where solid solutions are not formed. Oxygen-free copper, however, has a slightly higher recrystal-lization temperature than tough-pitch copper.

An increase in recrystallization temperature generally indicates an increase in work hardenability and this accounts undoubtedly, in part, for the strengthening effects of many of the low-concentration constitu-ents such as arsenic, antimony, and silver. Most published data regard-ing improvement in physical properties is on work-hardened mate-rial so that it is not usually possible to distinguish between specific strengthening effects of the alloying elements and secondary effects on work hardenability.

Silver increases the recrystallization temperature out of propor-tion to other effects. The purest copper may have a recrystallization temperature not much over 100°C, but this may be raised to be-tween 350° and 400°C by 0.5% silver.

QUESTIONS AND PROBLEMS

1. Why is copper more likely to be found in the native state than most other structural metals?

2. Calculate the percentage of copper in each of the minerals of Table 1, page 259.

3. Give definitions for blister copper, matte, flapping, poling, tough-pitch copper.

4. If it takes 96,550 coulombs to deposit electrolytically 1 gram atomic weight of a univalent metal from solution, how many ampere-hours should be required to electrolyze 1000 lb of copper, using a copper sulphate solution as an electrolyte?

5. List five nonelectrical applications of copper and state the characteristics made use of in each.

6. What is the resistivity (ohms per cubic centimeter) of copper that has a conductivity of 102.3% IACS?

Ans. 1.6854 × 10^{-6} ohms per cubic centimeter.

7. What is the resistance of a wire weighing 1 gram and 1 meter long and of conductivity equal to 100% IACS, if the density of the wire is 8.92 grams per cubic centimeter?

8. If the thermal conductivity is 0.923 calories per cubic centimeter per degree C per second, calculate the constant for the equation on page 264, using electrical conductivity of 100% IACS. Then calculate the thermal conductivity for copper of 102.3% IACS electrical conductivity.

9. What other element is necessary to promote the attack of acetic acid on copper? Is copper generally soluble in dilute acids?

10. Can you find any relationship between the solid solubility and the effect of an element on conductivity of copper?

11. In what other connection has a reaction similar to the one on page 271 been studied?

12. How are the conditions of Question 1 often defeated by combinations of alloying elements?

13. What elements generally improve the tensile properties of copper?

CHAPTER XXIV

Copper: Metallography

Structure of Cast Copper · Microstructure of Cold-Worked Copper and Annealed Copper · Twinning in Copper Crystals · Grain Size and Recrystallization Temperature · Effect of Cold Reduction and Recrystallization on Mechanical Properties

Copper is an excellent material in which to study properties which can be considered as typical of metals in general, particularly face-centered cubic metals. It is easily melted and cast into convenient specimens for metallographic examination. It is hard enough to take a good polish, yet sufficiently ductile to be cold worked to any degree. It exhibits noticeable work hardening when cold worked and this effect can be removed by annealing. It can be etched in both alkaline and acid etching reagents.[1] It has every conceivable kind of equilibrium relation with other metals, both in liquid and solid states.

Structure of Cast Copper

The structure of cast copper is usually coarsely crystalline with pronounced ingotism, i.e., columnar grains extending inward from the cooling surface (Figure 24.1).

A finely crystalline border and equi-axed crystals in the center portion indicate the cooling conditions in the different regions of the ingot. The chilling effect of the mold at the surface causes a zone of the metal to be supercooled. In this zone crystallization can start at numerous locations, resulting in small equi-axed crystals. However, as soon as this first shell is formed, heat is extracted more slowly from the

[1] A convenient reagent for etching copper is one part strong reagent ammonia and three parts water with 3% H_2O_2, added a few drops at a time. The surface of the specimen should be swabbed frequently with cotton.

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FIGURE 24.1. Cross section of a small copper ingot, 3×.

FIGURE 24.2. Microstructure of cast copper, 100×.

remaining liquid and a temperature gradient is set up in the liquid. Equilibrium is closely maintained between liquid and solid, and crystallization proceeds by growth of already formed crystals, no new nuclei being formed. These crystals grow in the direction of the temperature gradient, that is, toward the center, resulting in the columnar grains.

Possibly due to convection currents and to the temperature gradient becoming practically horizontal in the liquid, a time is reached when the tendency to form new crystals can again assert itself and equi-axed grains are again formed in the interior of the ingot.[2]

Under the microscope the grains are not featureless but show evidence of their dendritic origin (Figure 24.2). This is due to the presence of impurities, principally oxide as eutectic, which although small in amount have been segregated to the last portions of metal to solidify, viz., the interstices between the branches of the dendrites. The dark etching characteristics of this impure metal account for the visible dendritic pattern.

Microstructure of Cold-Worked Copper and Annealed Copper

Cold-worked copper shows the normal distortion and slipping of the crystal grains. Also the dendritic patterns appear crooked and wavy (Figure 24.3).

Upon reheating the cold-worked copper to above the recrystallization temperature, a complete revision of structure occurs. The cast crystal structure disappears completely and the dendritic patterns disappear, or are much less in evidence. This latter phenomenon may be attributed to solution and reprecipitation of the oxides into larger particles (same distinction as between troostite and visible carbide particles in spheroidite). The new structure consists of small equi-axed grains many of which are traversed by parallel bands of different luminosity or color (Figure 24.4).

Twinning in Copper Crystals

This banded pattern is the result of *stereo* or mirror symmetry between the crystallographic arrangements in different parts of the same crystal grain. This condition is known as *twinning* and pairs of adjacent bands are twins. Lines of contact between the twinned portions are the traces of twinning planes. In a twinning plane the atomic arrangement satisfies both of the symmetrical cubic arrangements.

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[2] A complete discussion and an analysis of the circumstances of crystallization are found in "Primary Crystallization of Metals," by F. R. Hensel, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.,* 124 (1937).

FIGURE 24.3. Microstructure of cold-worked copper, 100×.

FIGURE 24.4. Copper reheated after cold working, 100×.

In the face-centered cubic copper crystals the twinning plane is known as an octahedral or {111} plane (see Appendix II).

The twinning mechanism is shown in Figure 24.5. The twinning planes in the two eightfold face-centered cubic lattices are marked in heavy lines. Note that they are similar and parallel. The lower drawings show the corners of the two cubes matched together on the same twinning plane.
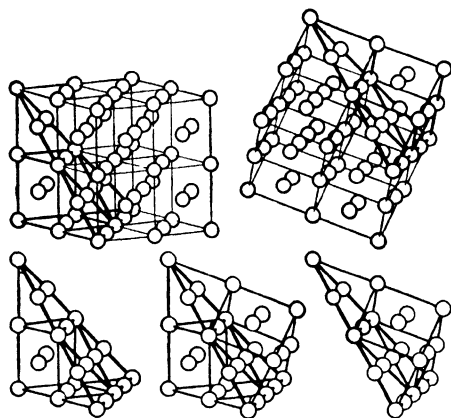
FIGURE 24.5. The twinning relation in face-centered cubic crystals.

These structures are useful in tracing the history of an article made of copper or a copper alloy. The cast structures are readily identified. Most rolled copper, brass, or bronze articles such as wires, bars, or tubes, are finished at low temperatures to secure greater strength and a fine surface finish. In general, the distortion of the grains is greater than that shown in Figure 24.3. In the case of wires it may be so severe as to leave only longitudinal striations visible in the microstructure. However, if twinned crystal grains are visible, we have positive evidence that the material has been heated subsequent to the cold working.

Grain Size and Recrystallization Temperature

The size of the grains in annealed or recrystallized copper is related not only to the actual annealing temperature but also to the previous condition of cold work, to the previous grain size (that is, prior to the cold work), to impurities in the copper, as noted before, and possibly to other factors not easily determined. The same is true for solid solution alloys of copper such as brasses, bronzes, and also other metals. For these alloys as well as for copper, the strength, hardness, workability, and other properties show marked variation in certain ranges of grain size so that a numerical estimate of grain size or grain count is important.

The simplest method of evaluating grain size is by comparison of a suitable photomicrograph with a standard chart such as that prepared by the American Society for Testing Materials (see *ASTM Standards*, 1946, vol. 1B, plate I, designation E2). Direct methods of making

grain counts are tedious and somewhat difficult, particularly where the twinning is pronounced. There is a question whether the twinned portions should be counted as separate crystals. Any answer leads to some inconsistencies but, generally, they are not counted.

In cold drawing of copper wire or cold rolling of copper sheet, work hardening occurs. In the case of very pure copper or some of the solid-solution alloys, the working and reduction can be continued indefinitely without rupture although the power required becomes high. With most copper it is desirable to process anneal occasionally; this results in recrystallization and softening. The recrystallization temperature is defined as that at which the formation of equi-axed grains first becomes noticeable under the microscope. It is usually slightly higher than the first softening temperature although close to it.

Effect of Cold Reduction and Recrystallization on Mechanical Properties

After a reduction of a little more than 50% in area, pure or tough-pitch copper reaches practically its maximum hardness and strength, and these will not increase much more and even may drop off with further reduction. The curve in Figure 24.6 [3] shows the effect of cold working on various mechanical properties of annealed tough-pitch copper.

FIGURE 24.6. Effect of reduction of area on hardness and tensile properties of tough-pitch copper sheet (redrawn by permission from *Copper and Copper Base Alloys*, by Wilkins and Bunn, copyright, 1943, by Mc-Graw-Hill Book Co., Inc.).

In the drawing and rolling of wires and sheets, sizes are expressed by gage numbers. Various systems are in use. Most of them use small numbers for the large sizes and as the gage number increases the diameter or thickness diminishes. An exception is the system for steel music wire.

For copper, copper alloys, and other nonferrous metals and alloys

[3] From *Copper and Copper Base Alloys*, by R. A. Wilkins and E. S. Bunn, McGraw-Hill Book Co.

the Brown and Sharpe (B & S) gages are used most in the United States. Gage No. 36 represents a diameter of 0.005 inch and an increase of six in gage number reduces the diameter about 50%. At this rate the effect of unit gage-number change should be to divide the diameter by $2^{1/6}$ (or 1.1224). This does not quite fit, however, so that the gages are somewhat empirical. Since the cross-sectional area of wire is proportional to the square of the diameter, an increase of *three* gage numbers represents a reduction of 50% in area of section of wire.

Since (as noted in the preceding paragraph) a reduction of 50% in area results in nearly maximum hardness for tough-pitch copper, it is apparent that this is represented by about six B & S numbers in the case of sheet, or three in the case of wire. Copper reduced by cold working to such an extent is considered hard drawn.

Likewise, copper heated to 800°C is generally considered fully annealed, as further heating will change the grain size but will not accomplish much greater softening.

QUESTIONS AND PROBLEMS

1. Describe the conditions under which a second phase makes a metal brittle rather than strengthens it. Name three elements that produce this effect.

2. Describe the structural and phase changes that should take place in a copper-lead alloy containing 50% lead when it is cooled from a temperature of liquid homogeneity to room temperature. See Figure 25.4.

3. What is meant by the recrystallization temperature? To what other characteristics may it be related?

4. Is the long direction of columnar crystals necessarily the same as one of the crystallographic axes? Explain.

5. How do the slip lines in copper compare to those in alpha iron?

6. How many twinning planes may be found in one copper crystal?

7. How does a twinning plane differ from a grain boundary?

The Copper Alloys: Brass and the Bronzes

Importance of Copper Alloys · Metallography of Copper Alloys · Brass · Manufacture of Brass · Metallography of Brass · Commercial Brasses · Cold Working · Hot Working · Corrosion of Brass · Leaded Brass · Other Additions to Brass · The Tin Bronzes —Phosphor Bronze · Metallography of the Copper-Tin Alloys · Compositions and Properties · Uses of Bronze

Importance of Copper Alloys

The alloys in which copper is the predominating element rank next to the iron alloys in industrial importance. Although it is true that during the period of World War II the production of aluminum alloys rivaled and may have at times surpassed that of copper alloys, this was largely the result of wartime demands. The future will probably see increased use of the aluminum alloys; not, however, so much in competition with the copper alloys as in the expansion of their own fields of usefulness. The many unique characteristics of copper alloys assure them a demand as long as metals are used.

The reasons for the universal popularity of copper alloys are quite obvious and are listed in the following paragraphs.

1. *Ease of Production.* Everything considered, it probably requires less special skill and equipment to produce the structural copper alloys than is required for other alloys of comparable character. One reason for this is the melting temperature which, being usually less than 1900°F, is easily attained. Another contributing factor is the nobility of copper, whereby it combines feebly with oxygen and is easily

deoxidized. Many of the alloying elements such as zinc, aluminum, and beryllium act as their own deoxidizers. Again, most of the copper alloys can be rolled, drawn, spun, extruded, and hot or cold worked in various ways.

2. *Corrosion Resistance.* Many of the copper alloys are more resistant to various types of corrosion than copper itself, which is usually listed as a corrosion-resistant metal.

3. *Color.* The color of copper is unique among metals, the only other strongly colored metal being gold. Copper alloys can be made of a great variety of tints many of which are similar to gold or gold alloys. In addition to this, oxide colors can be formed, such as the patinas on bronze, which produce many striking and artistic effects on statuary, jewelry, and various kinds of decorative hardware.

4. *Many Other Uses.* There are copper alloys for many special uses such as low-friction alloys for bearings, alloys of high resilience for bells and gongs, alloys for springs, and alloys of high plasticity for rivets.

The various applications listed will be discussed at greater length in consideration of the specific alloys.

Metallography of Copper Alloys

A glance at the equilibrium diagrams for copper-zinc, copper-tin, and copper-aluminum (Figures 25.1, 25.2, 25.3) would give the impression that the metallography of copper alloys is tremendously complicated. Actually, this is not true, and although the copper alloys present a number of interesting structures and many metallographic peculiarities, it is a fact that these structures fall into a few well-defined categories so that there is a great deal of similarity between the different copper-alloy systems. Again, nearly all the useful copper alloys are solid solution alloys with the crystal lattice of copper, that is, face-centered cubic. Occasional alloys, such as Muntz metal, exhibit a beta phase of higher alloy content. In nearly all cases this beta phase is body-centered cubic.

Most of the practical studies on the copper alloys deal with such considerations as grain size, recrystallization temperatures and softening temperatures, tensile and elastic properties, and corrosion resistance. Each type of alloy has its own individual peculiarities like the season cracking of brass and precipitation hardening in some of the bronzes, but, in general, the metallography of copper alloys is that of single-phase materials.
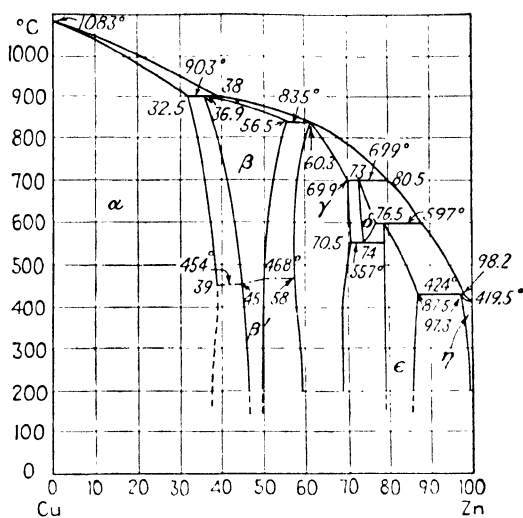
Per cent zinc	Phase	Temperature
32.5	Alpha	
36.9	Beta	903°C
38.0	Liquid	
56.5	Beta	
?	Gamma	835°C
60.3	Liquid	
69.9	Gamma	
73.0	Delta	699°C
80.5	Liquid	
76.5	Delta	
78.5	Epsilon	597°C
88.4	Liquid	
70.5	Gamma	
74.0	Delta	557°C
78.5	Epsilon	
87.5	Epsilon	
97.3	Eta	424°C
98.2	Liquid	

FIGURE 25.1. The copper-zinc equilibrium diagram (redrawn from *National Metals Handbook*, 1948). Table shows compositions at ternary points in diagram.

ALLOY SYSTEMS
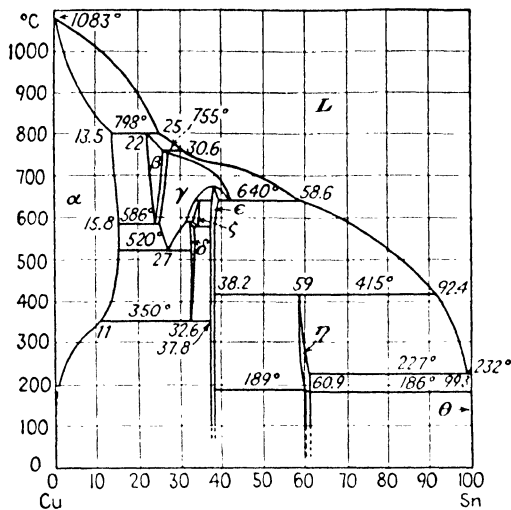
FIGURE 25.2. The copper-tin equilibrium diagram (tentative) (redrawn from *National Metals Handbook,* 1948, with data from various other sources).
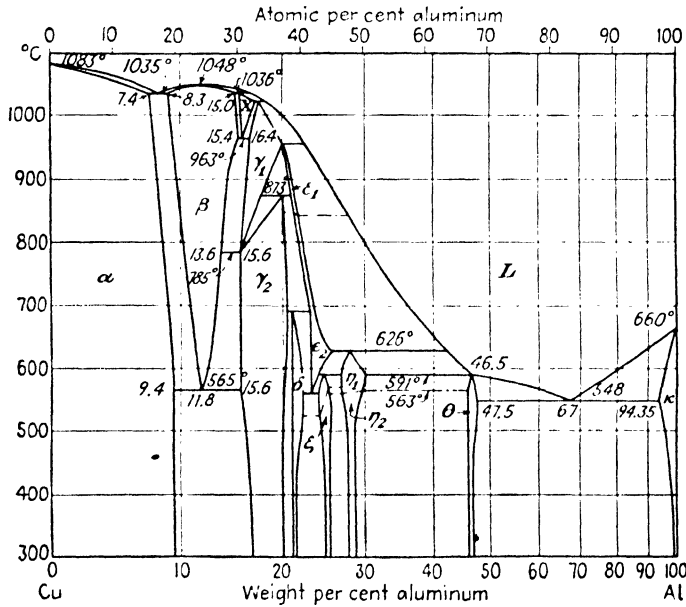
FIGURE 25.3. The copper-aluminum equilibrium diagram. (Values as given in the *National Metals Handbook.*) The construction between 16% and 50% weight of aluminum is generally speculative. Abscissas represent weight per cent values plotted to an atomic per cent scale. This is for the purpose of expanding the left portion of the diagram.

Brass

Brass is the name given to alloys of copper and zinc in which the color is quite different from that of copper. True brass contains very little of other alloying elements although the limits of composition are very indefinite. Occasionally one will find metals parading under the name of bronze that ought to be called brass, and vice versa. Probably the first claim of brass to importance is based on its color, which is quite like that of gold. Many gold alloys can be matched in color by selecting a brass of the proper composition.

Brass is a cheap alloy. In spite of the fact that zinc is wasted in the manufacture of brass, pound for pound it is cheaper than copper itself. This is, of course, due to the cheapness of zinc, which is usually mined in the form of sphalerite (sulphide of zinc, ZnS). Sphalerite is frequently found associated with lead ore and other more valuable minerals such as copper, silver, and gold.

Manufacture of Brass

The manufacture of brass is accomplished in many ways and in many types of furnaces, the complete description of which is beyond the scope of this text. New brass is usually made by first melting the copper and then adding the zinc. At the temperature of the molten copper, zinc is quite volatile and, as a result, a considerable portion of it is lost before the temperature can be lowered sufficiently to prevent its further escape. In making up a desired composition, allowance must be made for this volatilization and loss of zinc. This makes it quite difficult to meet exact specifications as to composition. It is particularly difficult to match colors in different melts.

Once the zinc is alloyed or in solution with the copper, however, the melting temperature of the alloy is lower and the tendency for the zinc to escape is lessened. Brass can be remelted with comparatively small zinc losses.

Metallography of Brass

Copper-Zinc Equilibria

The metallography of brass is comparatively simple. Referring to the equilibrium diagram for copper and zinc, Figure 25.1, we see at the left a large field representing compositions and temperatures of solid solutions of zinc in copper. This is the alpha solid solution range of the copper-zinc alloys. Alloys whose compositions lie within the limits of this field are referred to as alpha brass.

At ordinary temperatures annealed alpha brass may contain up to 39% zinc. This material is a solid solution having the same kind of space lattice as copper, that is, face-centered cubic. Due to the presence of the zinc, however, the lattice parameter (a_0) has increased to 3.70 Angstrom units. (The lattice parameter of pure copper is 3.61 A.)

In the annealed condition, alpha brass will have a tensile strength of from 40,000 to 50,000 psi, an increase of 50% over that of pure copper. The elongation and reduction of area, on the other hand, are not greatly different from the values for copper. This is characteristic of solid solutions. The strength may be increased without much loss and with even a gain in ductility.

Cold working, such as drawing into wire, may increase the strength of brass to over 100,000 psi. It thus makes a very useful structural alloy, the strength of which is comparable to that of steel.

Alpha brass has the crystalline characteristics of copper. If it is cold worked and then annealed, it will exhibit twinned crystals under the microscope, just like copper.

It is noteworthy that the liquidus and solidus in the alpha brass region lie close together. This signifies that during freezing there will not be a very great difference in composition between the liquid and solid. We should not, therefore, expect severe segregation in such alloys. As a matter of fact, they are comparatively free from segregation.

The properties of alpha brass vary almost linearly with composition so that brasses that have less than 39% zinc will have properties between those of pure copper and those of saturated alpha brass.

As shown by the diagram, when the zinc content exceeds the alpha range the equilibrium relationships become more complicated. At 903°C the alpha brass that is in equilibrium with the liquid starts to react with the liquid to form the beta phase. Beta brass is body-centered cubic and is harder and less ductile than alpha brass at low temperatures but more ductile and more easily worked at high temperatures.

At 835°C and 60.3% zinc, another peritectic point appears. Here the liquid reacts with the beta phase to form the gamma phase. Gamma brass has a complex space lattice that is similar to the body-centered cubic structure but can be described only in a block of twenty-seven simple body-centered cubes, that is, a cube whose edge is three times that of the simple cube. Such an arrangement would normally require 54 atoms per large cube. In the gamma brass unit cube, however, there are only 52 atoms, indicating that two atoms are missing from each cube. This would be expected to result in a highly strained lattice

which should account for the hard brittle character of gamma brass.

Gamma brass is white, as are the other phases of higher zinc content. With the exception of the eta solid solution of copper in zinc, alloys containing over 50% zinc have no commercial importance.

Effects of Heat Treatment in the Alpha-Beta Region

Again, note that the solvus curve that bounds the alpha field slopes to the right, as the left boundary of the beta field does also. This indicates that the alpha brasses can take more zinc into solid solution at lower temperatures. This has considerable structural and mechanical significance. If we draw a vertical line through the diagram at about 38% zinc and describe the progress in cooling of an alloy of that composition, we shall observe that after solidification is complete the alloy will consist (from 900°C to 800°C) entirely of beta brass. With slow cooling, alpha brass will form below 800°C. This increases in amount until, below 500°C, the alloy will consist entirely of alpha brass.

Although accomplished in a different manner, this is a transformation that is not unlike the change from gamma to alpha iron. The high temperature form (beta form) is the harder material in this case. Rapid quenching to room temperature will hold it in the beta form. From this condition the alpha phase starts upon moderate reheating to form either at beta grain boundaries or as a widmanstätten pattern within the grain. Low reheating temperatures in the neighborhood of 300°C will result in a partial transformation to an acicular or needle-like structure that is similar to the martensite of quenched steels. This seems particularly likely to occur if the beta phase has been put under strain by working.

The acicular structure has further similarity to the martensite of steel in that it contains a space lattice which, like the tetragonal lattice in steel, is different from either the alpha or beta brass and is transitory in nature, that is, it disappears at higher heating temperatures and crystal grains of alpha brass are formed. Matsuda[1] has shown that the acicular structure is considerably harder than the beta brass as quenched, or the alpha plus beta mixture formed at higher reheating temperatures. Thus it is similar to martensite in all respects, and this makes it perfectly correct to speak of martensitic structures in high brass and other alloys (of which there are several) that exhibit this characteristic.

The treatment discussed is not generally used to harden brass, for several reasons. In the first place, the maximum hardness of the mar-

[1] "On the Quenching and Tempering of Brass, Bronze, and Aluminum Bronze," by Tsutomu Matsuda, *J. Inst. Metals,* 29 (1928).

tensitic structure is not very great. The composition range in which the treatment is at all effective (38% to 42% Zn) is quite narrow. The quenching must be severe, and this would, of course, limit the treatment to thin sections or small pieces. Finally, for rolled or worked material, work hardening offers a much better and more easily controlled method of strengthening most brasses.

The Relationship of the Beta and Beta-Prime Forms

The change from the beta phase to beta-prime form has been observed as a halt or lag in the cooling curves for these alloys for many years. Only recently has it been demonstrated definitely to be the result of an ordering of the space lattice.[2] This means, in effect, that the copper atoms occupy the corners and the zinc atoms the centers of the body-centered lattice. This involves an energy change but is not generally considered to constitute an allotropic or phase change.

Commercial Brasses

On the basis of zinc content the brasses may be divided into three groups, namely, the low brasses, the high brasses, and the alpha-beta brasses. The low brasses contain less than 20% zinc, the high brasses from 20% to 39% zinc, and the alpha-beta brasses are usually exemplified by Muntz metal at 40% to 42% zinc.

Based on small percentages of components other than copper or zinc, another classification lists the leaded brasses, the tin brasses, and a number of special brasses such as nickel, aluminum, silicon, and arsenical brass. In all cases, the principal alloying elements are copper and zinc, the extra elements being in lower percentages than are usual in the corresponding bronzes. However, some of these alloys occasionally go by the name of bronzes, e.g., manganese bronze in which the manganese may be used only as a deoxidizer.

Table 1 lists some representative zinc brasses in order of zinc content and gives some of their applications. Table 2 lists some average physical properties for these compositions.

According to Table 2 the tensile properties of the alpha brasses approach maximum values at between 20% and 25% zinc. These maximum values are not changed much with increasing zinc content until the alpha-beta range is reached. This is, however, not the whole story, and a full understanding of the properties of the different brasses and of the reasons for selection on the basis of composition requires a

² See C. Sykes and H. Wilkinson, *J. Inst. Metals*, **61**, 223 (1937). Also see G. V. Raynor, *Annotated Equilibrium Diagrams Series*, *No. 3*, Inst. Metals (London), 1944.

TABLE 1. Some Commercial Wrought Brasses and Their Uses*

Common designation	Per cent zinc	Applications
Gilding metal.........	5	Imitation gold, jewelry, emblems
Commercial "bronze"..	10	Jewelry, weatherstripping, stampings, forgings, small hardware such as screws and rivets
Red brass.............	15	Cold drawing, spinning, stamping, automobile radiators, corrosion-resistant tubes and pipes
Low brass.............	20	Drawn and stamped articles, flexible hose; fair corrosion resistance; generally similar to red brass
Spring brass...........	25	Upper limit for best corrosion resistance; lower limit for springs and high-strength applications
Cartridge brass........	30	Best range for deep drawing; also called "70–30" and "deep drawing brass"
High brass............	34	Pins (domestic), rivets, musical instruments, electrical sockets, cartridge cases; excellent for deep drawing; cheap because of low copper content
Muntz metal..........	42	Representative of the alpha-beta brasses; highest tensile properties; best hot-working properties, architectural work; pipes, condenser tubes

* Condensed from similar tables by Wilkins and Bunn, *Copper and Copper Base Alloys*, and *National Metals Handbook*, 1939.

TABLE 2. Some Tensile Properties of Wrought Brasses (0.04-inch sheet) *

Designation	Zinc, %	Tensile strength, psi				Elongation ‡ in 2 in., %
		Soft †	Hard	Spring	Spring wire	
Gilding metal..	5	36,000	55,000	65,000		44
Commercial bronze......	10	38,000	64,000	73,000		45
Red brass.....	15	40,000	71,000	83,000		48
Low brass.....	20	43,000	75,000	91,000	120,000	55
Brazing or spring brass..	25	45,000	76,000	92,000	125,000	62
Cartridge brass.	30	46,000	76,000	92,000		64
High brass....	34	46,000	76,000	92,000	125,000	64
Muntz metal...	41	54,000	80,000 §			45

* Condensed from table by D. K. Crampton in *National Metals Handbook*, 1939, page 1397.   † Fully annealed.
‡ Values for elongation are on soft annealed material. These dropped to 3% on spring brass of all compositions.   § This value is for cold-rolled material.

knowledge of the effects of cold and hot working, a knowledge of corrosion and stress corrosion, understanding of another effect of chemical attack known as dezincification, and an appreciation of the effects of composition on the cost of the alloy.

Cold Working

All the alpha brasses can be cold worked by forging, rolling, drawing, or spinning, but the higher the zinc the less work hardening will occur. By work hardening is meant an embrittling effect that raises the yield point out of proportion to the ultimate strength. Actually, the high brasses can be made stronger and harder than the low brasses, but the high brasses retain some ductility even after severe working. This can best be explained by the existence of greater tenacity between unlike atoms of copper and zinc than between copper atoms only. Similar effects are observed in other solid solution alloys; noteworthy among these alloys are the nickel steels (see Chapter XX).

Brass containing less than 15% zinc must be frequently annealed at temperatures between 700° and 1500°F during cold working. Alpha brass with more than 15% zinc may be rolled or drawn indefinitely at room temperature.

The alpha-beta brasses are more difficult to cold work than the alpha brasses. Brass containing more than 42% zinc is practically unworkable at room temperature.

Cold working reduces the impact strength of brass, but this is presumably the result of lowered ductility.

Hot Working

The alpha brasses are, in general, more difficult to hot-work than to cold-work. At first this may seem odd in view of the fact that all brass may be successfully extruded. But extrusion involves only compressive stresses, whereas other methods of working involve stresses in tension. Thus we might conclude that brass at high temperatures is especially weak in tension. This is not surprising when we consider the high volatility of zinc.

Brass containing more than 20% zinc can be worked successfully at temperatures between 1350° and 1550°F. However, alpha brass must contain no lead, because minute amounts are ruinous to its hot workability. Muntz metal and the alpha-beta brasses, on the other hand, work quite well at high temperatures even when lead is present to the extent of 1%. This is explained, as far as the lead is concerned, by the fact that this much lead is soluble in solid beta brass.

Corrosion of Brass

If we analyze the reasons for the industrial importance of brass, we shall probably find that corrosion resistance is an essential factor in most of them. This refers not only to the direct application of the corrosion resisting characteristics such as in condenser tubes and plumbing fixtures, but also in the use of brass for ornamental purposes such as costume jewelry and decorative hardware. The fact that brass does not tarnish readily and that its effect is easily removed when corrosion does occur, probably has more to do with its use for decorative purposes than its color.

Cleaning of Brassware

The cleaning of low brass or gilding metal is easily accomplished with any commercial brass cleaner. Most cleaners contain ammonia or ammonia compounds whose function is to dissolve copper oxide. They also may contain fine abrasives, such as tripoli powder or crocus powder, whose action is purely mechanical. Compounds containing ammonia are questionable for cleaning high-zinc brasses because of the effect of the ammonia in causing season cracking.

Season Cracking and Dezincification

The two most damaging types of corrosion of brass are season cracking and dezincification. Season cracking is a form of stress corrosion and occurs in brass containing more than 15% zinc when such brass is under stress and exposed to ammonia vapor or mercury compounds or vapor. The stress may be external as in a tensed spring, or internal as the result of mechanical working. Season cracking can be inhibited by heating to just below the recrystallization temperature, but this is not always feasible.

The exact causes of season cracking [3] are not completely understood, but grain boundary attack by moist ammonia has much to do with it. The effect of mercury is even less well understood than that of ammonia. The alloying of the mercury with copper along grain boundaries with resulting weakening of these boundaries is the best theory so far.

Dezincification occurs in the higher brasses when they are exposed to salt or acid water. Sometimes water alkaline with ammonia may cause it. It is evidenced by a reddening of the brass, which is then found to be porous and weak.

[3] Symposium on *Stress Corrosion of Metals,* 1944, Joint Publication of American Society for Testing Materials and American Institute of Mining and Metallurgical Engineers.

Explanations of dezincification are based on the idea of a solution of the brass accompanied by a redeposition or plating out of the copper in a spongy mass. The zinc may either be removed in solution or form zinc oxide which remains as a chalky white material between the grains of copper. The microscope shows a variety of such structures depending upon the extent of dezincification and the medium causing it.

Arsenic, antimony, or phosphorus in small amounts tend to inhibit dezincification.

Leaded Brass

Lead is generally objectionable in brass that is to be worked, particularly if it is to be hot worked. Nevertheless, lead up to 3% or 4% is useful in brass to improve machinability and to render punching and shearing operations easier.

Reference to the copper-lead equilibrium diagram (Figure 25.4) shows lead to be practically insoluble in solid copper. The zinc-lead diagram (Figure 25.5) shows lead to be even less soluble in solid zinc than in copper. Consequently, it would be expected that lead should remain insoluble in brass. This is found to be true for alpha brass. However, body-centered cubic beta brass dissolves up to 1% lead in solid solution, and apparently this fact has a profound effect on the behavior of beta brass toward hot working, making such treatment feasible even when more than 1% lead is present.
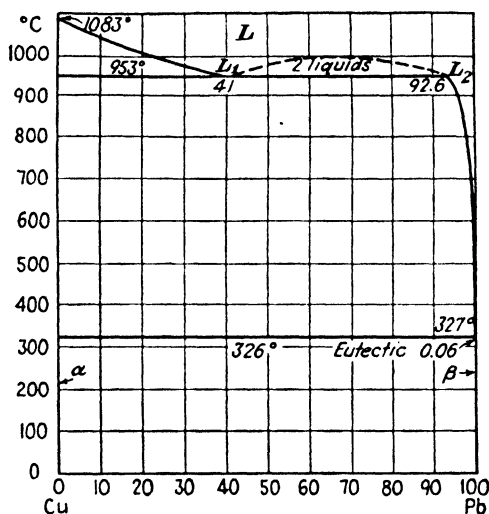
FIGURE 25.4. The copper-lead equilibrium diagram (redrawn from *National Metals Handbook*, 1948).

Compositions and Forms of Leaded Brass

The wrought leaded brasses parallel the straight zinc brasses in their zinc-copper ratio, but the commonly used specifications are for the high-zinc types with from 30% zinc up to the composition of Muntz metal (42% Zn). Hardware bronze containing 9% to 10% zinc and Lan-
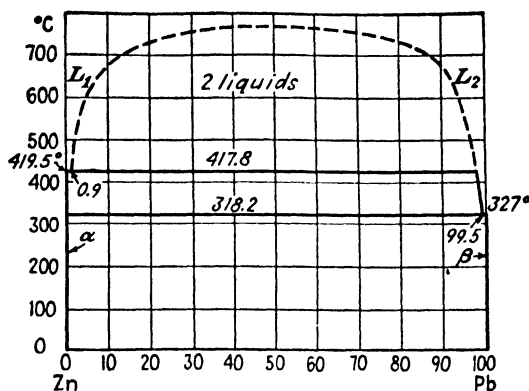
FIGURE 25.5. The zinc-lead equilibrium diagram (adapted from *National Metals Handbook*, 1948).

cashire brass with 24% zinc are representative of the lower zinc types. Lead varies from 0.50% to 4%. The tensile properties are quite similar to those for the corresponding zinc brasses except for somewhat lowered ductility when the lead exceeds 1%.

In the cast brasses, where workability ceases to be a consideration and machinability becomes important, lead up to 5% is used.

Metallography of Leaded Brass

As is the case with most copper-lead alloys, lead remains as droplets in leaded brass after the rest of the alloy has frozen. Reference to the copper-lead equilibrium diagram (Figure 25.4) indicates that practically all the copper solidifies before the copper-lead eutectic forms. The eutectic is practically pure lead (0.06% Cu), so that, in an alloy that contains up to 97.4% lead, the lead is segregated throughout the freezing range of the system. Ordinarily this would be expected to result in an unusable mass consisting of a copper shell filled with lead. Under certain conditions of cooling such an aggregate can form, but it is not the usual case.

The monotectic reaction at 953°C would be expected to intensify the tendency to segregate. Here, when the liquid from which copper is crystallizing reaches 41% lead, a new liquid forms which contains about 92.6% lead. The new liquid is heavier than the first one and sinks to the bottom. Very little copper separates from the lead-rich liquid on subsequent cooling so that it forms a sizable pocket of lead deep within the casting.

However, this rather dismal picture of the progress of solidification of the copper-lead alloys is not encountered in practice. For the

lower-lead compositions the growth of interlacing dendrites, coupled with reasonably rapid cooling, results in a finely divided lead phase. For high-lead copper-lead alloys the two liquids form an emulsion when cooled from above 1000°C. This causes one of the liquids to be divided into such small droplets that general segregation cannot occur.

Other Additions to Brass

Other elements that may be added in small quantity to brass are tin, nickel, aluminum, silicon, manganese, iron, and arsenic. These have specific effects in improving corrosion resistance, resistance to dezincification, tensile properties, and weldability. However, most of them have adverse effects upon workability so that their use is limited in wrought brasses.

Tin is added up to 2% to give greater resistance to corrosion. Probably the most important of the tin brasses is Admiralty metal which contains 30% zinc and 1% tin. This has become a standard alloy for condenser tubes. A tendency toward dezincification in Admiralty metal is overcome with small additions of arsenic. Because of its damaging effect on workability, tin does not exceed 2% in any of the wrought brasses and in the high brasses it is generally under 1%. Tobin bronze or Naval brass, with about 39% zinc, contains 0.75% tin.

Wrought manganese bronze is essentially an alloy of the Muntz metal type to which tin is added. It also contains up to 0.50% manganese and varying amounts of aluminum, iron, lead, and other impurities. Cast manganese bronze may or may not contain tin.

Table 3 gives the composition ranges for three representative manganese bronzes.

The manganese, iron, and aluminum all act to increase the tensile strength, which may reach 115,000 psi in the high tensile alloy. Iron and manganese also act to keep the grain size small.

TABLE 3. Manganese Bronzes Analysis

Component	Composition, per cent		
	Wrought type	Cast type	Cast type (high tensile)
Copper...............	55–60	55–60	64–71
Zinc.................	Balance	38–42	19–22
Tin..................	0.5–1.5	1.5 max.	0.02 max.
Manganese............	0.50 max.	3.5 max.	3.5–4.5
Iron.................	0.8–2.0	0.4–2.0	2.0–3.0
Aluminum.............	0.25 max.	1.5 max.	4.5–6.0
Phosphorus...........	0.20 max.	0.40 max.	0.02

Silicon up to 1% is added to brass that is to be spot or seam welded. Two brasses are made for this purpose. One contains 22% and the other 29% zinc. They find special use in refrigerators and evaporators.

Nickel, replacing zinc in zinc-copper alloys, forms the nickel-silvers. Most compositions range from 60% to 66% copper with nickel and zinc each varying from 5% to 30%. With increase of nickel the brass color is rapidly diminished, resulting in alloys varying from a pale bronze color to white. Most of these alloys originally were called German silver. International complications plus more widespread production caused the name to be changed. If now, popular animosity should be directed toward the lunar metal, perhaps a truly descriptive name might be evolved for these useful alloys which are neither German nor silver-bearing.

The nickel-silvers have excellent cold-working properties, rather poor hot-working properties, high strength and hardness, and excellent corrosion resistance. They are frequently used for articles that must withstand handling, such as clasps, handles, scientific instruments, and fishing reels. In industrial applications such as condenser tubes, they have strength and corrosion resistance superior to brass.

The Tin Bronzes—Phosphor Bronze

Bronze is the term that is applied to practically all alloys of copper other than brass which retain some of the color of copper and in which copper is the predominating element. The most extensively used bronze is tin bronze, and the term bronze, unless otherwise modified, signifies tin bronze. However, we also have aluminum bronze, beryllium bronze, silicon bronze, and a number of others. Some brasses are called bronzes, such as the Tobin bronze and manganese bronze noted in preceding paragraphs.

Most of the elements that form bronzes with copper have a considerable range of solid solubility in the face-centered cubic alpha phase. In this condition, as with brass, the color and ductility are retained up to a fairly high concentration of the solute. Also, as with brass, when the saturation concentration of the solute is exceeded, a new beta phase is formed which is harder than the alpha phase and makes the alloy amenable to heat treatment. This second phase is usually body-centered cubic.

Manufacture of Tin Bronze—Phosphor Bronze

The manufacture of tin bronze consists of merely melting the constituents together in any furnace available. There is no loss of tin nor does the tin protect the copper from oxidation as zinc does, and it is usually necessary to deoxidize the melt before casting. The most

popular element for this purpose is phosphorus, which is introduced as a high phosphorus-copper master alloy (phosphor-copper) which contains 10% or 15% phosphorus. Residual, unoxidized phosphorus in ·the bronze may vary from 0% to 0.5% according to specification. When present in noticeable amount it increases the hardness and strength of the bronze.

Bronze deoxidized with phosphorus, whether or not any remains in the metal, is called phosphor-bronze. The term phosphor-bronze therefore means tin bronze deoxidized with phosphorus.

Metallography of the Copper-Tin Alloys

The copper-tin equilibrium diagram of Figure 25.2 is now fairly well established. Because of its complexity much of the middle portion was long in dispute but modern methods of study have resulted in quite accurate and reproducible data throughout. This diagram is the one given in the 1948 National Metals Handbook. The original source was the diagram compiled by G. V. Raynor in *Annotated Equilibrium Diagrams Series, No. 2* of The Institute of Metals, London, 1944.

In contradistinction to the narrow range of solidification of the copper-zinc alloys (Figure 25.1), the copper-tin alloys have a wide space between the liquidus and solidus curves in the region below 25% tin. This indicates a serious tendency toward dendritic segregation and cored grains. This is one of the chief difficulties encountered in cast bronze. According to the diagram, the saturation value for tin in the alpha solid solution should be about 16%. Yet, because of dendritic segregation, or *coring*,[4] the alpha phase in a rapidly cooled alloy may average as low as 5% tin (see Chapter VII). Only by very slow cooling or by long annealing at 500°C can the concentration of tin be increased above 10% in the alpha phase.

As a further result of this severe coring, cast copper-tin bronzes are never homogeneous even when composed entirely of the alpha phase. In higher-tin alloys a phenomenon known as inverse segregation occurs. This is evidenced by the appearance of the delta phase. Presumably this is more noticeable near the surface of the casting where cooling was rapid than at the center where it was slow and the resulting structure more uniform. This would give the appearance of higher tin at the surface than at the center.

The boundary of the alpha phase area recedes rapidly to the left below 520°C. Below 350°C, where the alpha-epsilon eutectoid is

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[4] Crystals that show marked variation in composition, from center to surface, are sometimes called *cored* crystals.

shown to form from the delta phase, the alpha phase boundary recedes still more rapidly and appears to approach the copper vertical at room temperature. The phase that separates at low temperatures is the epsilon phase, a hard, brittle, intermetallic compound. It would seem likely that precipitation hardening effects should occur as a result of this behavior. On diagrams depicting the effects of reheating cold-worked alloys, some hardening effects are often shown in the neighborhood of 300°C, but the effects are not great enough to be of industrial importance.

As a matter of fact, the receding boundary of the alpha region is not easily demonstrated. Earlier diagrams showed a vertical line at about 16% tin, extending downward from 510°C. The microstructure of a bronze containing 8% tin is that of a single-phase alloy. Possibly the precipitation effect is not desirable and may help to account for season cracking in bronze; the Liberty Bell is a case in point.

The beta-gamma-delta relationships are complicated. They are all high-temperature phases and under equilibrium conditions should be resolved into alpha and epsilon at room temperature. However, at ordinary cooling rates the delta phase usually persists down to room temperature.

A most unusual and interesting phenomenon occurs in copper-tin alloys of a little over 40% tin. During the progress of cooling of an alloy containing, say, 41% tin, the following sequence occurs. Solidification commences with the formation of gamma crystals at about 715°C. At slightly below 700°C freezing is complete, the alloy consisting entirely of the gamma phase. At about 650°C the eta phase starts to form from the gamma phase until 640°C is reached. At 640°C the residual gamma phase decomposes to form, simultaneously, liquid and eta phases. This is an invariant point, there being three phases present, but it is apparently the only case known in metal systems where a solid alloy melts as the result of cooling. No name is given this type of reaction but it behaves like a peritectic reaction upside down.

Compositions and Properties

Wrought bronze compositions range from 2% tin to about 8% tin. They may be cold worked readily but hot working is usually confined to alloys containing less than 2% tin. Hot rolling may be applied to the 4% alloys. The strength of bronze increases with tin content and the 8% bronze when drawn into wire may show a strength of 130,000 psi. Values of from 100,000 psi to 110,000 psi are common for strip and rod.

The corrosion resistance of bronze is excellent and toward atmospheric corrosion it develops the gray-black patina that is admired in statuary.

Uses of Bronze

Springs

One of the most important uses for wrought bronzes of the alpha solid solution type is in the manufacture of springs. Bronze seems admirably adapted to this purpose for the following reasons. It has the low value for Young's modulus that is characteristic of copper alloys. This value is in the neighborhood of 15,000,000 psi and about half of that for steel, which means that it stretches elastically about twice as much for a given load as does steel. The high tensile strength and high fatigue limit of bronze place it ahead of most other copper alloys as a spring material. Its excellent corrosion resistance, lower tendency toward season cracking, and freedom from the dezincification that occurs in the high brasses make it superior to them. However, the combination of tin and zinc in bronzes, whereby the zinc does not need to be so high to secure the tensile strength, is also found to make excellent spring material. The advantage of such a combination probably lies in lower cost resulting from the incorporation of the cheaper zinc into the alloy.

Bearings

The chief commercial use for cast bronze is in bearings where its low coefficient of friction, high heat conductivity, high strength, and high melting temperature offer a combination of properties not matched in other alloys. It is particularly useful where high bearing pressures are involved such as in bushings and thrust bearings.

Lead is usually added to the cast bearing bronzes in amounts up to 10%, a common type containing 80% copper, 10% lead, and 10% tin. This bronze will usually have some of the delta phase present, due to segregation in the casting. The lead will, of course, be present as discontinuous globules as in all copper-lead alloys. This combination of hard and soft phases is usually sought in bearing metals as it seems to provide both supporting surface and channels through which the lubricant is properly distributed.

Wrought bearing and bushing bronzes may contain up to 2% lead and usually some zinc. A standard composition popularly known as gun metal contains 88% copper, 10% tin, 2% zinc, and 0.3% lead.

Industrial Castings

There is a great variety of specifications for industrial castings of bronze with varying amounts of elements, such as zinc, lead, nickel, cadmium, iron, and silicon, in addition to copper and tin. These have many uses such as plumbing fixtures, valves, marine engine parts, connecting rods, and propellers. A noteworthy specification is that of *ounce metal* consisting of 85% copper, 5% tin, 5% zinc, and 5% lead. It is especially adapted to castings that are to withstand hydrostatic pressure.

Since workability is not a factor in castings, there are almost no limitations to the compositions that may be used and the number of copper-base casting alloys is very great.

Bell Metal

Bells constitute an application of bronze that is by no means trivial. Besides church bells, chimes, annunciator bells for schools and hospitals and various institutions, dinner bells for farms, and long-to-be remembered sleigh bells, nearly all moving machinery, from locomotives and street cars to cranes and various devices in industrial plants, is guarded by bells.

Most of these bells are made of bronze. The best sound is secured at about 20% tin with varying amounts of zinc and lead. Such a high tin content will of course result in a two-phase bronze containing considerable of the delta or eta constituent. This makes a brittle alloy and great care must be taken in casting and annealing to avoid damaging strains.

Statuary Bronze

This may contain 5% to 10% tin and as much as 10% lead. It may also contain zinc. The lead is probably helpful in producing the gray-black patina that is characteristic of bronze statues.

QUESTIONS AND PROBLEMS

1. List characteristics in which aluminum alloys and copper alloys do not compete.

2. Describe the structural changes that occur in a brass containing 36% zinc when it is slowly cooled from the molten condition to room temperature. Do the same for a brass containing 38% zinc and for one containing 40% zinc.

3. If the face-centered alpha phase precipitates in planes parallel to the {110} planes of the body-centered beta phase, how many plane directions should the alpha phase have in a single beta crystal?

4. If the body-center atoms were all zinc and the corner atoms were all copper, what should be the formula for beta brass?

5. Why can low brass be cold worked if annealed occasionally, whereas it cannot be hot worked so easily at annealing temperatures?

6. What are the principal purposes of adding lead to brass? of adding arsenic? .

7. Why should a low-zinc brass be recommended for rivets whereas 30% zinc brass is said to be best for deep drawing?

8. Explain why lead should be "ruinous" to the hot workability of alpha brass.

9. From an elementary chemistry text find out what forms when CuO dissolves in ammonia, and write the reaction.

10. Suggest a reason why silicon improves the weldability of alpha brass.

11. In what kind of brass and under what conditions is season cracking most likely to occur?

12. Suggest a reason why dezincification of brass is more likely to occur than detinification of bronze.

13. What nonmetallic element has the property of melting at slightly over 100°C and resolidifying at a higher temperature? How does this differ from the behavior of the 40%-tin bronze?

14. Give three applications in which tin bronze should be superior to brass and give reasons in each case.

CHAPTER XXVI

Aluminum Bronze and Other Bronzes: a Correlation of Phases

Qualifications of Aluminum Bronze · Copper-Aluminum Equilibrium · Compositions and Properties · Heat Treatment · Other Copper Alloys · Beryllium Bronze · Phase Similarities and Replacement Values · Analogies in Crystal Structure · The Electron-Atom Ratio

Qualifications of Aluminum Bronze

The copper-aluminum bronzes have intrigued manufacturers of copper-base alloys since aluminum has been commercially available. Their strength is comparable to that of medium-carbon steel. Their values for elongation and reduction of area compare favorably with those of steel. Their corrosion resistance is superior to that of manganese bronze. Their color is the finest of all the copper alloys, and they are frequently called imitation gold. They make suitable bearing alloys. They have excellent hot-working characteristics through a wide temperature range (1300°–1700°F), which is rare for copper alloys. While they can be cold worked, they work-harden severely which makes them unsuited to stamping and drawing.

From the above considerations one might conclude that aluminum bronzes should be superior for most purposes to the brasses or tin bronzes. Yet, for ample reasons, they are less generally used than the older alloys.

They present serious problems in casting. Having high liquid shrinkage, they tend to pipe. This requires large discards from ingots

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and large risers for castings resulting in low production efficiency. A dross forms on the surfaces of ingots and castings. In the case of ingots that are to be rolled, this dross must be removed by machining. In castings, care must be taken that it is not folded into the interior to form damaging discontinuities.

Aluminum bronze tends to season-crack like brass, and exhibits dealuminization, similar to the dezincification of brass. It is somewhat difficult to machine, possibly because of the abrasive properties of entrapped aluminum oxide.

Copper-Aluminum Equilibrium

The copper-aluminum equilibrium diagram (Figure 25.3) presents a sequence of phases similar to the other copper-alloy systems. This includes the face-centered cubic alpha phase, body-centered cubic beta phase, and a complex body-centered cubic gamma (or delta) phase with 52 atoms per unit cube. The beta field contracts to a eutectoid point at 565°C. Between the composition of the gamma (or delta) field at 18% aluminum, and that of the compound $CuAl_2$ at about 47% aluminum (53% copper), the diagram is not well established and, as there are no commercial alloys in this range of composition, the range has only theoretical interest.

Rapid quenching does not suppress the beta-eutectoid transformation, and martensitic structures result. In fact, at temperatures just below the eutectoid temperature, the transformation is similar to that of steel even to the formation of intermediate space lattices, similar to the tetragonal lattice of the steel martensite. The aluminum bronzes respond much more strongly to quenching and tempering than do the brasses or tin bronzes.

Compositions and Properties

While the equilibrium diagram shows about 9.4% aluminum to represent the limit of the alpha field, alloys that contain more than 7.5% aluminum will be composed of alpha and beta phases, under ordinary conditions of cooling. Such alloys respond to heat treatment. Those containing less than 7.5% aluminum do not. Thus, there are two principal types of commercial aluminum bronzes. One contains about 5% and the other from 9% to 11% aluminum. The 5% alloy constitutes the imitation gold for jewelry. Table 1 lists a few alloys used commonly.

Heat Treatment

Heat treatment of the alpha aluminum bronzes is confined to annealing and stress relieving treatments. The tensile strength, yield strength,

TABLE 1. Wrought Aluminum Bronzes

Analysis, per cent			Tensile properties			Treatment
Cu	Al	Fe	U.t.s., psi	Elongation in 2 in., %	Reduction of area, %	
87	10	3	103,000	13	17	Air cooled
92	7	1	126,000	7.5	35	Cold rolled
92	7	1	81,200	45	62	Annealed— 1300°F
86.5	10.3	3.2	102,900	12.7	* 17.2	Water- quenched from 1650°F, tempered at 1000°F
88*	9	3	80,000	30	30	As rolled
95*	5	0.5	60,000	30	30	As rolled

* Standard compositions.

and Rockwell hardness values drop sharply upon annealing to temperatures between 600° and 700°F. Elongation and reduction of area increase sharply in this same range. With cold-worked 5% bronze, the change in tensile strength between annealing temperatures of 600° and 700°F is from 120,000 psi to 70,000 psi. Above 700°F the drop in strength is very gradual and a value of 60,000 psi will be maintained after annealing at 1300°F. Annealing temperatures below 600°F slightly increase the strength of the cold-worked material.

Noticeable increases in grain size of the alpha bronzes occur between 700° and 900°F, the exact temperature of incipient grain growth depending upon the previous condition of cold work.

The heat treatment of the higher, alpha-beta aluminum bronze consists of quenching from between 1500° and 1600°F and tempering to some temperature between 700° and 1100°F. Such treatments are effective in improving the properties of the cast aluminum bronzes. However, as with the brasses and tin bronzes, cold working seems to be a more effective way of controlling the properties of the wrought aluminum bronzes than straight heat treatment.

Other Copper Alloys

The enumeration and complete description of all the copper-base alloys is the subject for a rather extensive handbook. It is hoped that such a handbook will be forthcoming soon. The three systems selected for this text have been chosen to show similarities in structural and

phase relationships and to exemplify the processes of compounding alloys generally. Closely allied diagrams will be found for the copper-beryllium, copper-cadmium, and copper-silicon alloys. With these elements silver forms systems that are somewhat similar to the copper alloys. The equilibrium diagram for the copper-nickel alloys is shown in Figure 7.1 and illustrates solid solubility in all proportions. There are many special alloys of copper and nickel including the cupro-nickels, Monel metal, and various alloys for electrical use. Table 2 lists some representative examples of the more important copper alloys that have not been discussed here. Under the heading "Type" is listed the type of equilibrium diagram that most closely describes the system. Some of these are simple types like the simple eutectic system of the lead-tin alloys; others are complex like the copper-zinc and copper-tin systems. Under "Maximum tensile strength" is listed the maximum *useful* value that can be obtained for each alloy.

TABLE 2

Alloy	Type	Maximum tensile strength, psi	Chief advantage in use
Cu + 2.5% Be	Complex	175,000	High strength, corrosion resistance, heat treatability
Silicon bronze (Cu + 1% to 3.25% Si)	Complex	110,000	Weldability ,
Cupro-nickel (Cu + 20% to 30% Ni)	Solid solution (Type VI)	85,000	Corrosion resistance (salt water)
Constantan (Cu + 45% Ni)	Solid solution (Type VI)		Electrical resistance, high thermoelectric effect
Monel metal (Cu + 65% Ni)	Solid solution (Type VI)		Corrosion resistance against chemicals
Silver solder (80% Cu; 15% Ag; 5% P)	Eutectic; partial solid solubility (Type II)		Brazing copper and brass

Beryllium Bronze

The beryllium bronzes have attracted much attention in recent years. They have tensile properties far superior and corrosion resistance at least equal to those of any other copper alloys. They can be heat-treated in much the same manner as aluminum alloys. The chief obstacle to their more general use is their cost, since beryllium is a comparatively scarce element and is likely to continue to be such.

Also the cost of reduction of the metal from the mineral beryl ($3BeO\text{-}Al_2O_3\text{-}6SiO_2$) is rather high. Beryl is the mineral that in pure crystalline form composes emeralds, aquamarines, and other gem stones.

Phase Similarities and Replacement Values

Considering the equilibrium diagrams for the copper-zinc, copper-tin, and copper-aluminum alloys, similar phase sequences are noted in all three systems. Physical properties of alpha phase alloys are related to the solid solubility of the second element in the alpha phase. The maximum physical values are obtained at saturation values of the solute. This was observed in an earlier chapter for the gamma phases in chromium, molybdenum, and tungsten steels. As with the steels, a replacement or substitution value can be assigned to each solute element of the alpha copper alloys. This value is proportional to the saturation value of the solute element and indicates the relative amount of each element that will bring the physical properties to some determined value. Thus, if the replacement value for aluminum is 1, that for tin is about $1\frac{1}{2}$, and for zinc 4. Such a scheme is, of course, only roughly approximate, but it serves as a convenient method of estimating possible compositions for experimental alloys.

Analogies in Crystal Structure

Another consideration is the similarity in structures of the corresponding phases in the different systems.[1-4] If, on an *atomic* per cent basis, we plot the equilibrium diagrams for the copper-zinc, copper-tin, silver-cadmium, and a few other systems of a monovalent plus a divalent metal, we will notice a degree of regularity in the composition ranges of the alpha, beta, and gamma phases. Furthermore, the alpha phase is face-centered cubic, the beta phase is body-centered cubic, and the next phase (whether or not it be called gamma) has a complex body-centered cubic structure with 52 atoms per unit cube. If there is a phase corresponding to the delta copper-zinc, or epsilon copper-tin, it is usually hexagonal close packed. Similar sequences of phases are found in many other alloys such as copper-aluminum, iron-zinc, and cobalt-zinc.

[1] *Structure of Metals*, by Charles S. Barrett, McGraw-Hill Book Co., 1943.

[2] "Structure Analogies of Alloys," by Arne Westgren, *Trans. Am. Soc. Steel Treating*, 20:6, pp. 507–528 (December, 1932).

[3] *The Structure of Metals and Alloys*, by Sir William Hume-Rothery, Monograph, Institute of Metals (London), 1936.

[4] A. L. Norbury, *J. Inst. Metals*, 65, 355 (1939).

The Electron-Atom Ratio

William Hume-Rothery made the first consistent correlation of these structures and noted that when the ratio of the number of valence electrons to the number of atoms approached certain values, the composition would lie within the range of homogeneity of one of the phases listed above. The valence electrons are taken as those outside the last completed shell of each atom. On this basis the electron-atom ratio for the beta phase is 3:2; for the gamma phase, 21:13; for the epsilon (delta brass) phase, 7:4.

As examples, the beta brass solid solubility range lies on both sides of the CuZn composition. The valence of copper is 1, that of zinc is 2, so the 3:2 ratio holds. On the other hand, Cu_5Sn lies within the beta copper-tin range, but tin has a valence of 4. Here the electron-atom ratio is 9:6 which again equals 3:2.

In the gamma phase the formula Cu_5Zn_8 occurs in the range of homogeneity of gamma brass, which fits the 21:13 ratio for the complex cubic structure; in the copper-tin system the analogous phase is delta with a composition that closely approximates $Cu_{31}Sn_8$. Here the electron-atom ratio is 63:39, that is, 21:13.

This rule has been found to hold for a great many other alloys and is useful in prophesying structures, not only in binary systems but also in those of multiple components. The valences that may be applied to the elements in following this rule are listed in Table 3.[5]

TABLE 3. Elementary Valences of Some Alloying Elements

Valence	Element
0	Fe, Co, Ni, Ru, Rh, Pd, Pt, Ir, Os
1	Cu, Ag, Au
2	Be, Mg, Zn, Cd, Hg
3	Ga, Al, In
4	Si, Ge, Sn, Pb
5	P, As, Sb, Bi

Studies by Norbury[6] indicate that the 21:13 ratio is too simple in some cases and he has been able to obtain closer correlations by assuming three slightly differing ratios for the gamma phases.

QUESTIONS AND PROBLEMS

1. What is the quickest and simplest way to distinguish aluminum bronze from gold?

2. Of what does the dross on aluminum bronze mostly consist? Why is it difficult to eliminate?

[5] By permission from *Structure of Metals*, by Charles A. Barrett, copyrighted, 1943, by McGraw-Hill Book Co., Inc.
[6] *Loc. cit.*

3. Describe the phase changes that should occur when aluminum bronze containing 10% Al is cooled from the molten condition to room temperature.

4. What differences can you suggest between the eutectoid for aluminum bronze and the eutectoid for steel that might account for the greater effectiveness of heat treatment of steel?

5. Compare maximum values of tensile strength for brass, tin bronze, aluminum bronze, and beryllium bronze. Give the two most important characteristics to be considered in the selection of each.

6. Calculate the percentage of the second component in the formulas $CuZn$, Cu_5Sn, Cu_5Zn_8, Cu_3Al, Cu_3Sn_x, Cu_9Al_4. How well do these fit the ranges of homogeneity of the beta and gamma phases as shown on the equilibrium diagrams?

CHAPTER XXVII

Aluminum and Aluminum Alloys

History · Occurrence of Aluminum · Refining Difficulties and Impurities · Metallography of Pure Aluminum · Properties of Pure Aluminum · Aluminum Alloys · Metallography of Aluminum Alloys —Etching Chemistry · Heat Treatment · Artificial Aging · Alloying Elements · Binary Equilibrium Relationships · Classification of Commercial Aluminum Alloys · Mechanical Properties · Specific Effects of the Alloying Elements · Complex Aluminum Alloys · The Mechanism of Age Hardening

History

Although aluminum is the most plentiful metallic element in the earth's crust, it has been available as a metal only in modern times. The first proof of its existence seems to have been made by Sir Humphry Davy in 1807.[1] He was unable to obtain it in sufficient purity to investigate its properties. However, he obtained it in metallic form alloyed with iron and was able to recognize its presence. Oersted[2] in 1827, and Wöhler in 1828, produced aluminum and studied its properties. From 1854 to 1859 interest again developed in aluminum, and by 1860 it was produced on a small commercial scale in England by a man named Gerhard. It sold for 3 shillings 9 pence (about 95¢) an ounce.

Modern aluminum production started with the Hall process which was developed in the 1880's. By the turn of the century aluminum had become an established article of commerce. Today it vies with copper for second place in the list of useful metals.

[1] *The Playbook of Metals,* Pepper; Book List, No. 99, Appendix IV.
[2] "Aluminum," *Encyclopaedia Britannica.*

Occurrence of Aluminum

Aluminum occurs in a wide variety of minerals. These can usually be resolved as a combination of aluminum oxide with oxides or compounds of other elements. For instance, the feldspar orthoclase ($KAlSi_3O_8$) can be written $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. An exception is cryolite ($NaAlF_4$). The principal constituent of ordinary clay is kaolin whose formula is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. A hard, crystalline form of alumina (Al_2O_3) is corundum. This is a common mineral but occurs in gem form as clear crystals in rubies and sapphires.

The mineral bauxite is a whitish claylike material composed of aluminum oxide and varying amounts of combined water. Large deposits of it occur which contain only minor amounts of impurities. Bauxite is plentiful, cheap, and widely distributed, and is almost the sole mineral from which metallic aluminum is produced. It is usually uneconomical to employ mechanical or chemical concentration methods on less pure aluminum minerals.

The oxygen is held so tenaciously in alumina that ordinary smelting methods will not work. The early methods of production sought to reduce it by means of metallic sodium or potassium, although it may be said to the credit of Sir Humphry Davy that, in 1807, he saw the possibilities of the electric current and used it in his experiments.

Charles M. Hall solved the problem of cheap production of aluminum by discovering that molten cryolite ($NaAlF_4$) could serve as a solvent for aluminum oxide, forming therewith an electrolyte in which the aluminum oxide could be decomposed by the electric current. The cryolite remained intact.

Refining Difficulties and Impurities

Because of its high oxidation potential there is no simple way of refining aluminum by oxidizing the impurities, as is done in steel manufacture and in copper smelting. Practically all purification must be effected in the ore prior to its electrolysis, or by special electrolytic purification processes such as the Hoopes process. (In the Hoopes process the aluminum is first alloyed with some copper and then electrolyzed. The molten pure aluminum floats on the electrolyzing bath while all impurities stay on the bottom with the copper.) When once the aluminum metal, during ordinary melting or casting operations, becomes alloyed or contaminated with other metals, it remains that way. Aluminum scrap becomes less pure after remelting because oxidation of some of the aluminum concentrates the impurities in what is left.

Commercially pure aluminum contains from 0.30 to 1.00% of impurities, most of which are iron and silicon. These have noticeable effects on the physical properties.

Metallography of Pure Aluminum

Aluminum has a face-centered cubic space lattice with a lattice constant $(a_0) = 4.0413$ A. The lattice content for copper is 3.6080 A. The microstructure of cast, cold-worked, and annealed aluminum is quite similar to that of copper. There is, however, no eutectic formed with aluminum oxide as between copper and copper oxide so that the grains of cast aluminum do not show dendritic markings.

The twinning mechanism occurs in aluminum that has been annealed after cold work, and straight sided bands traverse the aluminum grains just as they did in the case of copper. This phenomenon is characteristic of all face-centered cubic metals.

The color of the etched aluminum surface is usually light gray and varies in intensity from grain to grain if the etching has been deep. This is due to roughening of the surface with minute etching pits whose effects vary as the orientation of the grains with respect to the polished surface varies.

Properties of Pure Aluminum

The purest aluminum has a freezing temperature of 660°C. However, the value usually given for aluminum of high commercial purity (Alcoa 2S) is about 658°C. Pure aluminum is very soft and ductile with a tensile strength as low as 8500 psi. The electrical conductivity, on a volume basis, is 64.94% IACS, which is equivalent to about twice the mass conductivity of copper.

Corrosion Resistance

In pure aluminum this is high in spite of the high affinity of aluminum and oxygen. The explanation is the thin tight film of Al_2O_3 that forms instantaneously on the surface of aluminum whenever it is exposed to air. This film, which is only a few molecules thick, apparently inhibits further oxidation. While most oxidizable metals, including iron and copper, inhibit their own oxidation in a similar manner, aluminum maintains its resistance to attack in the presence of dampness and some corrosive liquids. Indeed, strong mineral acids (HCl and HNO_3) can be transported in aluminum containers.

The reasons for the exceptional corrosion resistance of aluminum are not entirely known although part of the effect is probably due to the fact that Al_2O_3 is colorless and does not seriously impair the luster

of the aluminum. The oxide layer will adsorb certain dyes, and aluminum articles can be colored thereby.

Alclad

The corrosion resistance of pure aluminum is better than that of most of its alloys. A process has been developed by which wrought aluminum alloys in sheets, wires, tubes, or shapes, are coated with a thin layer of pure aluminum to improve their corrosion resistance. Such material is called alclad and the process of applying the coating is referred to as *cladding*. Actually, several processes are used, including aluminum metal spraying, but the common process consists in rolling the alloy at elevated temperatures between two sheets of pure aluminum. The aluminum sheets become firmly welded to the alloy.

Density

The low density of aluminum is perhaps its most significant qualification for industrial importance. This, for the purest metal, is 2.6989 grams per cubic centimeter. Most alloying elements raise the density, at least with the first additions, although light elements like magnesium and silicon lower it when present as separate phases.

Coefficient of Linear Expansion

For pure aluminum this is about 24×10^{-6} per degree C in the 0°–100°C range. For many purposes it would be advantageous to have aluminum alloys with the same coefficient of expansion as cast iron (10.5×10^{-6}).[3] For instance, aluminum pistons for internal combustion engines have the advantage of lightness and consequently give low energy losses as reciprocating parts. Much effort has been spent, and with some success, in producing an aluminum alloy whose coefficient of expansion is reasonably close to that of the gray-iron engine cylinders so that such pistons can maintain their close fit to the cylinders at any temperature at which the engine is likely to be run.

Aluminum Alloys

Since the invention of the Hall process much time and effort have been spent by the producers of aluminum in developing useful alloys. The objectives have been the usual ones such as high tensile properties, high fatigue limits, and high impact values, together with good workability or casting properties, machinability, and corrosion resistance. Special alloys for special purposes have been developed, including the low-expansion alloys noted, alloys for rivets, and alloys suit-

[3] *National Metals Handbook;* Book List, No. 47, Appendix IV.

able for such special processes as spinning, die casting, extrusion, and impact extrusion. Over sixty different standard specifications are now listed although these represent but a fraction of the total number of aluminum alloys that have been used.

The production of aluminum has been in the hands of comparatively few producers and as a result the development of these alloys has been systematically and intelligently directed. There has been little overlapping of effort, and the market has not been crowded with an incomprehensible list of specifications, as in the case of ferrous and copper alloys where each one is extolled by its advocates to the exclusion of all others.

However, it should be pointed out that the technology of aluminum alloys is really simpler than that of the iron and copper alloys. The heat treatment of the aluminum alloys is always based on one mechanism which is somewhat simpler than that for iron or copper, inasmuch as it is not complicated by changes in the crystal lattice of the solid-solution matrix. This matrix is always face-centered cubic aluminum, and hardening is almost entirely a matter of fineness of dispersion of precipitated alloy phases. The only exception lies in the earliest stages of the hardening process, at which point the exact mechanism is still a matter for controversy.

Metallography of Aluminum Alloys—Etching Chemistry

There has been worked out a rather elaborate system of etching reagents by which various intermetallic phases in aluminum alloys can be distinguished and identified. The reader should consult standard handbooks [4] and texts [5] for complete information concerning such etching reagents and the system of identification. The policy of elaborating on metallographic technique has been avoided in this text, but because it throws light on the chemistry of aluminum, a brief discussion of the principles involved in etching aluminum specimens will be presented.

The ingredients used in these etching reagents are principally hydrofluoric, hydrochloric, nitric, and sulphuric acids, and sodium hydroxide. The hydrofluoric acid has a mild solvent effect on the aluminum but sometimes stains it. Its effect on silicon and silicon-bearing constituents varies from almost no visible effect on pure silicon particles to various degrees of staining on silicon compounds. Possibly it has a solvent action on the pure silicon but does not roughen or stain it

[4] *The National Metals Handbook;* Book List No. 47, Appendix IV.
[5] *Principles of Metallographic Laboratory Practice,* Kehl; Book List, No. 16, Appendix IV.

and thus causes it to appear lighter in color as the etched aluminum matrix darkens.

The mineral acids act in various ways but usually the concentrations necessary to penetrate the protective layer of aluminum oxide are too high for smooth, clean etching. Best results are secured by using mixtures of these acids with hydrofluoric acid. Sulphuric acid has somewhat of a solvent effect on the Al_2O_3 and is used in some of the acid mixtures. Nitric acid in organic solvents like alcohol or glycerin is used to distinguish some of the alloy phases.

Sodium hydroxide has the most direct solvent action on Al_2O_3 and aluminum, forming sodium aluminate (Na_3AlO_3). Its action on most of the alloy phases is slight. The fact that aluminum is attacked by both acid and alkaline reagents is helpful in making possible a rather complete system of phase identification.

Heat Treatment

The hardening of aluminum alloys by heat treatment is well exemplified by a consideration of the aluminum end of the aluminum-copper equilibrium diagram (Figure 27.1).[6]

The solvus curve, extending from 5.65% copper at the eutectic temperature of 548°C to 0.1% copper at room temperature, shows that the solid solubility drops off very rapidly between the eutectic temperature and about 300°C. The phase that separates from the aluminum-rich solid solution is a solid solution whose narrow composition range includes the molecular formula $CuAl_2$. This compound is hard and, when present in finely divided form, stiffens the aluminum matrix to produce an alloy of considerable hardness and tensile strength.

FIGURE 27.1. The aluminum end of the copper-aluminum equilibrium diagram (adapted by permission from *Metallography of Aluminum Alloys*, by L. F. Mondolfo, published by John Wiley and Sons, Inc., 1943).

The heat-treated aluminum-copper alloys contain less than 5.65% copper (usually between 4.0% and 5.5% copper). The process of heat treatment consists of heating to a little over 500°C, quenching in cold

[6] Metallography of Aluminum Alloys, Mondolfo; Book List, No. 97, Appendix IV.

water, and aging for about two days at room temperature. By that time the material will have acquired maximum hardness and strength through the formation of a fine precipitate of $CuAl_2$ particles.

With pure aluminum-copper alloys it is not desirable to hasten the aging by heating to above room temperature, as maximum strength will not be obtained. Apparently the particle size increases beyond the optimum size for hardening. The fact of greater solubility of $CuAl_2$ at elevated aging temperatures is probably not significant because, at any temperature likely to be used, the solubility is still too slight to affect noticeably the amount of $CuAl_2$ available for precipitation.

Artificial Aging

By the addition of other elements to the aluminum-copper system, alloys are obtained in which precipitation takes place more sluggishly. Such alloys are aged in the neighborhood of 200°C with good results. The aging time is shorter and the product has higher strength than is obtainable in the simpler alloys. This higher temperature aging is called artificial aging to distinguish it from room temperature aging.

Alloying Elements

While copper is the principal alloying element in the very useful series of alloys known as the duralumins, a number of other elements, either singly or in groups, form useful alloys with aluminum. A list of these and the maximum percentages used in aluminum alloys is given in Table 1.

TABLE 1.   Maximum Percentages of Various Elements
Used in Aluminum Alloys

Element	Maximum per cent	
	Wrought alloys	Cast alloys
Silicon...............	12.5	12.5
Zinc.................	5.6	11.0
Copper..............	5.5	10.0
Magnesium...........	5.2	10.0
Nickel...............	2.0	2.0
Manganese...........	1.2	2.0
Bismuth..............	0.5	
Lead.................	0.5	
Chromium...........	0.3	
Tin..................		6.5
Iron.................		1.2

Silicon and iron in amounts up to 0.5% are found as impurities in practically all aluminum alloys. The silicon is advantageous in nearly all cases. Iron is usually kept to as low a value as possible.

Binary Equilibrium Relationships

The binary equilibrium diagrams for aluminum with each of the metals listed in Table 1, excepting zinc, bismuth, lead, and chromium, show the same type of relationship on the aluminum side as is seen in the aluminum-copper diagram. There is an aluminum-rich solid solution that attains its highest concentration of the alloying element at a eutectic temperature. This concentration limit drops off rapidly at lower temperatures and has a very low value at room temperature. The phase that separates from the solid solution upon cooling is either an intermetallic compound or the element itself. In all alloys excepting those with bismuth and lead, the precipitated phase hardens the aluminum matrix. With bismuth and lead two liquids are formed, in a manner similar to that of the copper-lead system, resulting in a *monotectic* point where the two liquids are in equilibrium with solid aluminum.

In Table 2 are summarized the data obtained from the equilibrium diagrams for aluminum with each of the elements listed.

TABLE 2. Equilibrium Data for Aluminum Alloys

Alloy system	Precipi-tate phase	Solid solubility, per cent *			Eutectic composi-tion, %	Eutectic tempera-ture, °C
		Maximum	At 300°C	At room tempera-ture		
Al-Si	Si	1.65	0.01	0.01	11.7	577
Al-Zn	99% Zn	84.0	35.0	2.0	96.0	382†
Al-Cu	CuAl₂	5.65	0.50	0.10	33.0	548
Al-Mg	Mg₅Al₈	17.4	6.7	1.4	33.0	449
Al-Ni	NiAl₃	Low			5.7	640
Al-Mn	MnAl₆	1.82	0.20 (ca.)	0.05	1.95	658
Al-Bi	Bi	0.20			3.36‡	657‡
Al-Pb	Pb	0.20			1.52‡	658‡
Al-Cr	CrAl₇	0.87	0.15 (ca.)		0.41§	661§
Al-Sn	Sn	20.0		2.0	99.0	229
Al-Fe	Fe₂Al₇	0.03	0.01		1.8	655

* Per cent of second component.
† See diagram, Figure 27.2.
‡ Monotectic point, two liquids formed.
§ Peritectic point.

Bismuth and Lead

These are used in aluminum alloys to improve machinability. When the aluminum freezes they remain as liquid particles until a much lower temperature is reached. For pure lead this is 327°C, and for pure bismuth 271°C, but when used together they can form a eutectic that freezes at 125°C. Lead expands on melting and thus may cause cracking on hot working. Bismuth contracts on melting and, when used in conjunction with lead, overcomes the cracking tendency.

Aluminum-Zinc

The diagram, Figure 27.2,[7] shows a eutectoid at 77.7% zinc and 275°C.
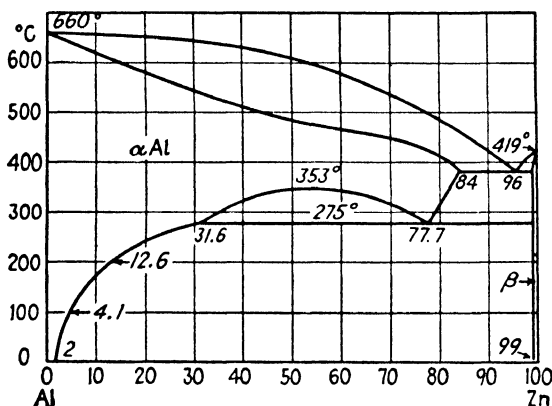
Figure 27.2. The aluminum-zinc diagram (revised) (redrawn with slight changes from Mondolfo).

Classification of Commercial Aluminum Alloys

The classification listed by the Aluminum Company of America is given in Table 3.[8] This system is chosen because it is most familiar to users of aluminum in the United States and because it encompasses about all the types of alloys of aluminum that are likely to be encountered. More complete information may be found in specification listings of the Army, Navy, SAE, ASTM, and Bureau of Standards.[9]

[7] *Metallography of Aluminum Alloys,* Mondolfo; Book List, No. 97, Appendix IV.

[8] *ALCOA Aluminum and Its Alloys,* Aluminum Company of America, 1946, 1947; Book List, No. 85, Appendix IV.

[9] *Mechanical Properties of Metals and Alloys,* U. S. Bureau of Standards, Circular 447; Book List, No. 43, Appendix IV.

Number 142, also called the Y alloy, has had considerable popularity in Europe.

It will be noted that numbers for the wrought alloys are followed by the letter S. Additional symbols are as follows:

T   Fully heat treated and age hardened, either at room temperature or above room temperature.

W   Solution treated but not aged. For alloys that do not age harden at room temperature.

RT   Cold worked after heat treatment.

T   Followed by a number (e.g., T–3), refers to certain modifications of the usual heat treatment or strain hardening process.

Wrought alloys in the soft or fully annealed condition are indicated by the letter O following the specification number. Strain-hardened alloys are indicated by the letter H preceded by a fraction, as in Table 4.

TABLE 3.   Standard Aluminum Alloys

A. WROUGHT ALLOYS

Alcoa symbol	Nominal composition (% of alloying elements)				
	Cu	Si	Mg	Mn	Others
2S					1.00 max.
3S				1.2	
4S			1.0	1.2	
11S	5.5				Pb, 0.5; Bi, 0.5
14S	4.4	0.8	0.4	0.8	
17S	4.0		0.5	0.5	
A17S	2.5		0.3		
18S	4.0		0.6		Ni, 2.0
24S	4.5		1.5	0.6	
25S	4.5	0.8		0.8	
32S	0.9	12.2	1.1	1.0	Ni, 0.9
43S		5.0			
A51S		1.0	0.6		Cr, 0.25
52S			2.5		Cr, 0.25
53S		0.7	1.3		Cr, 0.25
56S			5.2	0.1	Cr, 0.10
61S	0.25	0.6	1.0		Cr, 0.25
63S		0.4	0.7		
72S					Zn, 1.0
75S	1.6		2.5	0.2	Cr, 0.3; Zn, 5.6

TABLE 3 *(Continued)*

B. CAST ALLOYS

| Alcoa symbol | Nominal composition (% of alloying elements) | | | | Type of casting * |
	Cu	Si	Mg	Others	
13		12.0			D
43		5.0			S, PM, D
85	4.0	5.0			D
108	4.0	3.0			S
A108	4.5	5.5			PM
112	7.0			Zn, 1.7	S
113	7.0	2.0		Zn, 1.7	S, PM
C113	7.0	3.5		Zn, 2.0; Fe, 1.2	PM
122	10.0		0.2		S, PM
A132	0.8	12.0	1.2	Ni, 2.5	PM
D132	3.5	9.0	0.8	Ni, 0.8	PM
138	10.0	4.0	0.3		PM
142	4.0		1.5	Ni, 2.0	S, PM (Y Alloy)
195	4.5	0.8			S
B195	4.5	2.5			PM
212	8.0	1.2			S
214			3.8		S
A214			3.8	Zn, 1.8	PM
B214		1.8	3.8		S
F214		0.5	3.8		S
218			8.0		D
220			10.0		S
319	3.5	6.3			S, PM
355	1.3	5.0	0.5		S, PM
356		7.0	0.3		S, PM
360†		9.5	0.5		D
380†	3.5	8.5			D
384	3.8	12.0			D
750	1.0			Ni, 1.0; Sn, 6.5	PM

* S = sand; PM = permanent mold; D = die.

† The alloys A360 and A380 have the same nominal compositions as 360 and 380 respectively, but the impurities, notably iron, are controlled to closer limits.

Mechanical Properties

Quite comprehensive data on the mechanical properties of all these alloys are obtainable from the manufacturers and other sources. A sample list is given in Table 5.

Specific Effects of the Alloying Elements

From a survey of Table 2 and various physical property tables it is observed that the elements that are most effective in hardening, or

TABLE 4. Relation of Strain Hardness Designation
to Per Cent Cold Reduction [10]

Symbol	Designation	Approximate reduction of area by cold work, %
O	Soft or annealed	0
$\frac{1}{4}$ H	Quarter hard	21
$\frac{1}{2}$ H	Half hard	37
$\frac{3}{4}$ H	Three-quarters hard	60
H	Hard	80

TABLE 5. Mechanical Properties of a Few Aluminum Alloys [11,]

Alloy	Temper designation	Tensile strength, psi	Yield stress, psi	Elongation in 2 in., %	Type of product
2S	O	13,000	5,000	35	
2S	H	24,000	21,000	3	
17S	RT	65,000	47,000	13	
24S	T	68,000	44,000	19	
52S	As rolled	31,500	21,000	22	Sheet
52S	H	41,000	36,000	8	Rod
75S	T	76,000	67,000	11	Sheet
75S	T	80,000	70,000	6	Extruded
43		19,000	9,000	6	Sand cast
43		24,000	9,000	9	Perm. mold cast
43		30,000	14,000	7	Die cast
220	T4	46,000	25,000	14	Sand cast
122	T65	48,000	36,000	0.5	Perm. mold cast

otherwise altering the properties of aluminum, are those that have appreciable solid solubility in the aluminum at high temperatures and retain a small but definite solubility at room temperature. This applies to copper, silicon, magnesium, manganese, zinc, and tin. Tin does not seem to have as much effect as its solubility would appear to warrant, but the data on tin is meager and not too well established. The scarcity of tin makes it unlikely to be an important alloying element with aluminum.

[10] *Mechanical Properties of Metals and Alloys*, U. S. Bureau of Standards, Circular 447; Book List, No. 43, Appendix IV.
[11] "Aluminum," *Encyclopedia Britannica*.
[12] *Alcoa Aluminum and Its Alloys;* Book List, No. 85, Appendix IV.
[13] *Mechanical Properties of Metals and Alloys*, U. S. Bureau of Standards, Circular 447; Book List, No. 43, Appendix IV.

Copper

The most important and effective of the above named elements are copper, silicon, magnesium, and zinc. All the high-strength aluminum alloys contain one or more of these in considerable quantity. The mechanism of precipitation from solid solution is probably the principal factor in controlling the properties of such alloys, yet each element introduces some distinctive characteristics of its own.

Probably more study and research has been devoted to the aluminum-copper relationships, and particularly to the mechanism of age hardening of the aluminum-copper alloys, than the others, because until recently they formed the basis for the alloys of highest strength, namely the duralumins. However, with the development of the 75S alloy, zinc, which had been forsaken after an early start, received new recognition.

Zinc

At the turn of the century, zinc was considered to be the most important alloying element for aluminum. Later it was dropped because by itself it did not convey the combination of properties that were obtained in the duralumins. While it produced high-strength ductile alloys, in the quantities used it increased specific gravity, gave inferior corrosion resistance, produced hot shortness, and had a tendency to stress cracking. However, it is difficult to see why zinc in combination with other elements and in carefully controlled percentages should not yield some exceptionally valuable alloys.

Silicon

Silicon is the favorite for casting alloys. It is used sparingly in the wrought alloys, except in 32S which is for forging only. As a strengthener it is not spectacular. It seems to convey the characteristics that are wanting in zinc alloys. It reduces specific gravity, improves corrosion resistance, reduces hot shortness, and improves high temperature properties. In all commercial aluminum, some silicon is present and may exceed 0.5%.

While the solid solubility of silicon in aluminum is only 1.65% at the eutectic temperature, its solid solubility characteristics are good. That is, the solid solubility drops off rapidly at lower temperatures, making possible a finely dispersed silicon precipitate in the rapidly cooled alloy. However, the solid solution does not undercool to any great extent even on drastic quenching, so that age hardening is not pronounced in these alloys.

Strength in the aluminum-silicon casting alloys is the result of the finely divided eutectic aggregate. The diagram in **Figure 27.3** [14] shows the eutectic composition at 11.6% Si. Under ordinary conditions this eutectic is not very finely divided and does not form a particularly strong or hard alloy. However, a process of casting is used which produces a eutectic at about 13% silicon. This eutectic is almost submicroscopically fine.

Modification of Cast Aluminum-Silicon Alloys

The process known as "modification" consists of introducing 0.01% of sodium into the alloy at the time of casting. It may be introduced as metallic sodium in the mold, or as sodium fluoride, which is reduced by the aluminum with the formation of aluminum fluoride. The amount of sodium must be accurately controlled, as too much causes coarse particles of silicon to form and also embrittles the alloy.

There is no good explanation of the modification process although several theories have been advanced. The oldest one holds that the liquidus on the silicon side is depressed, so that the liquid becomes undercooled and supersaturated with respect to silicon. The finer eutectic then forms at the lower temperature and higher silicon content. The dotted lines on the diagram (Figure 27.3) illustrate this theory. Critics of the theory note that the rapid cooling obtained in permanent mold or die casting of straight aluminum-silicon alloys does not give the same degree or type of modification that is secured by the sodium. However, these methods do give more finely dispersed eutectics and greater strength than simple sand castings.

FIGURE 27.3. The aluminum-silicon equilibrium diagram (data from *National Metals Handbook*, 1939, and other sources).

Aluminum-silicon alloys have high electrical and thermal conductivity. For this reason they are especially suitable for steam radiators, waterjackets, manifold castings, and uses involving heat transfer. They are very fluid and cast well.

[14] *Metallography of Aluminum Alloys*, Mondolfo; Book List, No. 97, Appendix IV.

Magnesium

From the equilibrium diagram, Figure 27.4,[15] one would conclude that magnesium should form important alloys with aluminum; and this is true. The high solid solubility (14.9%) at the eutectic temperature with rapid drop to low solubility at room temperature, and the formation of the compound Mg_5Al_8 as a precipitate phase strongly suggest age-hardening properties. These are pronounced in aluminum-magnesium alloys. The lightness of magnesium promises alloys of low specific gravity, and the similarity in the melting temperatures of the two elements seems to indicate simplicity in melting. Although the last statement is not entirely borne out in practice, the difficulties are by no means insurmountable and aluminum-magnesium casting alloys have high popularity.

FIGURE 27.4. The aluminum-magnesium equilibrium diagram (compiled by permission from Mondolfo, as cited *sub* Fig. 27.1 *ante*).

However, like chromium in steel, magnesium performs its greatest service in conjunction with other alloying elements. With copper, silicon, and zinc it forms binary intermetallic compounds, and in the presence of aluminum and where several alloying elements are involved, magnesium appears in many ternary and quaternary combinations. Each of these combinations has distinctive relationships with the aluminum matrix, with the result that an almost unlimited variety of alloys is possible where magnesium is present.

Complex Aluminum Alloys

The discussion of equilibrium systems of more than two components is beyond the scope of this book, but for a comprehensive study of aluminum alloys, the available multiple component diagrams should be consulted.[16] A few of the intermetallic compounds that form in aluminum alloys are listed in Table 6.

[15] *Metallography of Aluminum Alloys*, Mondolfo; Book List, No. 97, Appendix IV.

[16] *Ibid.*

TABLE 6.   Intermetallic Compounds in Aluminum Alloys

Binary	Ternary	Quaternary
$CrAl_7$	$CrSiAl$	$CuFeAlSi$
$CuAl_2$	Cu_2FeAl_7	$CuMg_5Si_4Al_4$
Fe_2Al_7	$CuMg_4Al_6$	$FeMg_3Si_6Al_8$
Mg_5Al_8	$Cu_2Mg_2Al_5$	
Mg_2Si	$CuNiAl$	
$MnAl_6$	$FeSiAl_5$	
$NiAl_3$	$Mg_3Zn_3Al_2$	

Magnesium Silicide

In conjunction with silicon, magnesium forms a type of alloy with aluminum that illustrates a distinctive principle in binary equilibrium. The compound Mg_2Si forms with aluminum what is frequently referred to as a quasi-binary system. It is described as a vertical section through the three-component (Al-Mg-Si) diagram, and appears as a two-component diagram with aluminum at one end and Mg_2Si at the other. This binary system is shown in Figure 27.5. Actually, it is probably a true equilibrium diagram since Mg_2Si undergoes no decomposition within the limits of the system, and this qualifies it, according to phase rule definition, as a single component.

Magnesium silicide (Mg_2Si) is an excellent hardening constituent and requires elevated temperature aging. The formula Mg_2Si requires a ratio of magnesium to silicon of 12.16: 7.00. If the magnesium exceeds this, the solid solubility is rapidly reduced. Excess silicon, however, has no effect, and in most aluminum-magnesium silicide alloys the silicon equals or exceeds this ratio.
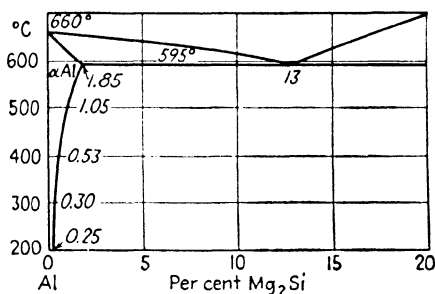
FIGURE 27.5.   The aluminum-magnesium silicide equilibrium diagram (redrawn by permission from Mondolfo, as cited *sub* Fig. 27.1 *ante*, and from *National Metals Handbook*).

Minor Components

Manganese is intentionally added to many of the aluminum alloys. Its effect is quite complex but can be described best by stating that it overcomes some of the damaging embrittling effect of iron (that is always present) by inhibiting the formation of quaternary phases com-

posed of aluminum, silicon, iron, with copper or magnesium. Just why the Al-Fe-Mn-Si phase that is formed is not equally damaging is not entirely clear, but it seems probable that it is less compatible, that is, has lower solid solubility in the aluminum matrix. This should result in the effect of its presence being proportional only to the comparatively small space that it occupies.

Manganese increases strength in cast aluminum-manganese alloys without significant loss in corrosion resistance. It prevents excessive grain growth and seems favorable to ductility in artificially aged alloys.[17]

Chromium, ·likewise, is a grain refiner. Its behavior is probably similar to that of manganese. It improves high-temperature strength.[18]

Nickel, because of extremely low solid solubility, acts in a mechanical way to increase strength. It maintains high-temperature strength and has practically no effect on conductivity.

Manganese, chromium, nickel, and beryllium as well, act as conditioning agents for aluminum. They "tone up" the alloys with regard to strength, high-temperature strength, and grain size without adversely affecting other properties.

Iron is the "bad boy" in aluminum and is usually kept at a minimum in the manufacture. However, it does increase strength at room and higher temperatures, and in combination with sufficient manganese to nullify its bad effects on ductility, it probably gives a net result that is beneficial.

The Mechanism of Age Hardening

A simple theory, based on slip interference by dispersed particles of a precipitate phase, has been found inadequate to explain all the phenomena attendant upon the aging of aluminum alloys. According to such a theory, hardening should commence at the first appearance of the precipitate. The precipitate will appear as a cloudiness or dark etching characteristic, similar to the troostite or sorbite of tempered steel. Higher temperatures coarsen this precipitate and ultimately cause the particles themselves to become distinguishable. Maximum hardness should either coincide with, or follow closely, the first appearance of this precipitate and the effect of further or higher temperature aging should be to reduce the hardness below the maximum.

However, in many alloys an increase in hardness occurs before there is any evidence of a precipitate. Moreover, changes in other physical

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[17] *The Heat Treatment and Annealing of Aluminum and Its Alloys,* Budgen; Book List, No. 92, Appendix IV.

[18] *Aluminum and Its Alloys,* W. G. Corson, Union Carbide and Carbon Research Laboratory, 1926.

characteristics of the alloy indicate that the increase in hardness is not coincident with the first appearance of the precipitate. Much research has been spent in the attempt to develop a complete theory of age hardening.[19]

In an exhaustive study on a duralumin of the 7S type, Morris Cohen[20] obtained a series of curves similar to the one shown in
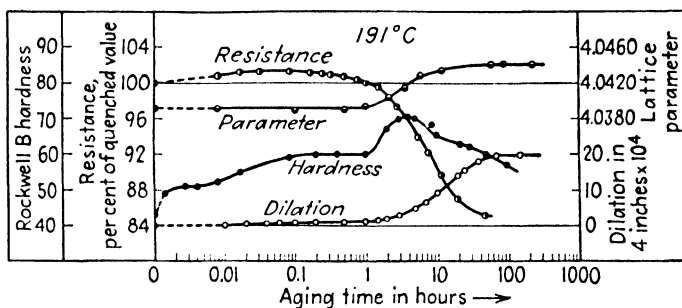
FIGURE 27.6. Aging curves of a duralumin alloy at 191°C (from "Age Hardening of Duralumin," by Morris Cohen, *Trans. Am. Inst. Mining Met. Engrs.,* 1939, page 100).

Figure 27.6. For this particular alloy, higher aging temperatures shifted the curves to the left so that some of the peaks, or humps, could not be observed because of too high a reaction rate. Lower temperatures, especially below 100°C, shifted the curves to the right to such an extent that time was not available for completion of the reaction. Work by Fink and Smith,[21] Gayler,[22] and others showed two aging peaks instead of three. At length, there was general agreement that the beginning of age hardening occurred in stages, and that each stage represented a different kind of change in the alloy. In Cohen's alloy

[19] "The Theory of Age-Hardening," Marie L. V. Gayler, *J. Inst. Metals,* **60**: 249 (1937). "On the Problem of the Age-Hardening of Duralumin," D. A. Petrov, *J. Inst. Metals* (1938). "Age-Hardening of Aluminum Alloys. III—Double Aging Peaks," W. L. Fink and D. W. Smith, *Trans. Am. Inst. Mining Met. Engrs.,* **128**: 223 (1938). "Age-Hardening of Duralumin," Morris Cohen, *Trans. Am. Inst. Mining Met. Engrs.,* Vol. 133, p. 95 (1939). "The Process of Precipitation from Solid Solution," Carl H. Samans, *Trans. Am. Inst. Mining Met. Engrs.,* Vol. 137, p. 85 (1940). "Age-Hardening of Aluminum Alloys. IV—Discussion of the Theory," W. L. Fink and D. W. Smith, *Trans. Am. Inst. Mining Met. Engrs.,* Vol. 137, p. 95 (1940).

[20] "Age-Hardening of Duralumin," Morris Cohen, *Trans. Am. Inst. Mining Met. Engrs.,* Vol. 133, p. 95 (1939).

[21] "Age-Hardening of Aluminum Alloys. III—Double Aging Peaks," W. L. Fink and D. W. Smith, *Trans. Am. Inst. Mining Met. Engrs.,* **128**:223 (1938).

[22] "The Theory of Age-Hardening," Marie L. V. Gayler, *J. Inst. Metals,* **60**: 249 (1937).

the electrical resistance increased during the first stage, reached a peak during the second stage, and diminished rapidly during the third stage. At the same time, the lattice parameter remained practically unchanged until the advent of the third stage. The dilatometer indicated a slight expansion in the first stage, followed by a slight contraction. During the third stage, both dilation and lattice parameter increased greatly as the electrical resistance decreased.

There now seems to be fair agreement among the various investigators regarding a general explanation of these changes. During solution treatment small groups of atoms, in which the ratio of the numbers of different kinds of atoms is just right for the precipitate phase ($CuAl_2$, etc.), are continually forming and disintegrating. When the alloy is quenched, these small groups, or "knots," are caught in the act of forming and held in place. Lowered thermal agitation prevents their disintegration. In the first stage of aging, the solute atoms in these knots become rearranged in a more regular pattern and form nuclei for the precipitate phase. Gayler believes that the solute atoms first congregate on certain crystallographic planes of the aluminum matrix.

The second stage is one of localized precipitation on grain boundaries. This has a noticeable effect on hardness but is not sufficiently extensive to affect other characteristics.

In the third stage, general precipitation occurs throughout the matrix and the microstructure shows darkening, or actual particles of the precipitate. This robs the matrix of the solute, resulting in increased conductivity (lowered resistance). It also accounts for the increased lattice parameter and for the dilation. The peak in hardness seems to occur just after the beginning of general precipitation.

QUESTIONS AND PROBLEMS

1. What is the hardness, on Mohs' scale, of aluminum oxide? Look up its melting point. Has it any uses in metallurgy?

2. The specific gravity of Al_2O_3 is about 3.75; that of cryolite (Na_3AlF_6) is about 3.00. What bearing do these facts have on the melting and refining of aluminum?

3. Taking the specific gravity of pure aluminum as 2.70, calculate the mass electrical conductivity as compared to copper from the value given in the text of 64.94% IACS on the volume basis.

Ans. Aluminum has 2.14 times the mass conductivity of copper.

4. From the values given on page 310 for the lattice constants of copper and aluminum and the maximum density of 8.953 given for copper in Chapter XXIII, calculate the density of aluminum. How does this result compare to the value given on page 311?

5. Aluminum-alloy rivets are frequently refrigerated and held at a temperature in the neighborhood of 0°F after quenching from the annealing temperature. What are the reasons for and purpose of this treatment?

6. From the data in Table 2, page 315, sketch partial equilibrium diagrams for the following systems: Al-Si; Al-Ni; Al-Mn; Al-Cr; Al-Sn; Al-Fe.

7. What advantage can you think of in modifying aluminum-silicon castings with sodium fluoride rather than with metallic sodium?

8. Suggest a reason why an excess of magnesium over the Mg_2Si composition should affect the solubility of Mg_2Si more than an excess of silicon.

9. How does the second stage of precipitation hardening account for a maximum in electrical resistance?

10. How does the general precipitation in the third stage account for increased lattice parameter and dilation?

CHAPTER XXVIII

Magnesium and Magnesium Alloys

History · Production Methods · Occurrence of Magnesium · Magnesium as a Metal · Crystallography of Magnesium · Magnesium Alloys · Tensile Properties · Corrosion · Alloying Elements · Metallography of Magnesium and Magnesium Alloys · Magnesium Alloy Specifications · Heat Treatment of Magnesium Alloys · Corrosion Resistance · Protective Treatments

The *lightest structural metal* is magnesium. To most people there is a definite sense of surprise when they first lift a bar or block of magnesium. It seems hollow or lighter than wood, certainly too light for any metal.

Actually, its specific gravity is 1.74 which is considerably denser than water and almost two-thirds as dense as aluminum (sp.g. = 2.70). Most alloying elements increase its density, although not very much in the quantities used, and magnesium alloys of considerable strength are but slightly denser than pure magnesium.

History

The history of magnesium is not as dramatic as that of aluminum, probably because it parallels but lags behind that of aluminum. Sir Humphry Davy [1] was unable to isolate the metal although he produced it in a mercury amalgam and demonstrated that MgO was its oxide. In 1828, Bussy prepared metallic magnesium by reduction with potassium of the fused anhydrous chloride. Bunsen produced the metal by electrolysis of the fused chloride in 1852. Sainte-Clair Deville and Caron reduced the anhydrous chloride with sodium in 1857. Their

[1] *The Technology of Magnesium and Its Alloys*, compiled by Dr. Ing. E. h. Adolph Beck (translation from the German), F. A. Hughes and Co., Ltd., London, reports this and other work cited in this chapter. (Book List No. 101, Appendix IV.)

process was used in Germany, England, and France, while Bunsen's electrolytic process was used in Germany. Early production was entirely for photographic and pyrotechnic purposes.

Production of magnesium alloys for structural purposes seems to have started in Germany about 1909. The Chemische-Fabrik Griesheim-Electron jointly with the Aluminium and Magnesium Fabrik promoted the series of "electron" alloys.

Under the stimulus of World War I, production was begun in the United States, notably by the Dow Chemical Company. However, it required a threat of aluminum shortage at the start of World War II to expand magnesium production to a large scale. Much of this expansion was under Government subsidy and for war purposes. At the present writing, the productive capacity in the United States exceeds the peacetime demand visible for several years. However, magnesium is a useful metal and the discovery and expansion of new applications for it should be a tempting field of endeavor for metallurgists and industrialists.

Production Methods

Present day production methods for magnesium are numerous and will not be dwelt upon here except to state some of the chemical principles involved. All the methods involving reduction by alkali metals (Na or K) have been replaced by electrolytic processes because such reduction methods are wasteful of energy that is mostly of electrolytic origin anyway. In addition, there are new methods that depend upon direct reduction with carbon, ferro-silicon, or aluminum. These methods are possible, in spite of the high stability of MgO or $MgCl_2$, because of the high volatility of the magnesium.

The principal difficulty encountered in the electrolytic methods is the problem of producing pure, anhydrous magnesium chloride. The $MgCl_2 \cdot 6H_2O$ produced by evaporation can be dehydrated by heating to form $MgCl_2H_2O$, but beyond this the following type of reaction occurs:

$$MgCl_2 \cdot H_2O = MgO + 2HCl.$$
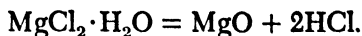
Actually the dehydration is not quite so complete as this, and the dryest chloride that can be produced by careful heating without loss of HCl corresponds to about $MgCl_2 \cdot 1\frac{1}{4}H_2O$.

Electrolytic Method

This material can be electrolyzed, but with some carbon-anode and power consumption, due to decomposition of the H_2O. However, it is probably the simplest electrolytic method.

Carbothermic Process

The reaction

$$MgO + C = CO + Mg$$
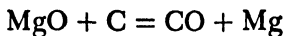
results in magnesium gas at temperatures above 1700°C, but the products of the reaction must be "shock" cooled in a blast of cold hydrogen to prevent reversal of the reaction. This forms the basis of the carbothermic production method.

Pidgeon Process

Reduction of the magnesium in dolomite by ferro-silicon or powdered aluminum-silicon alloys is the basis of the Pidgeon process.[2] Mixtures of calcined dolomite and the reducing agent are briquetted and heated in a retort to 1150°C. The retort consists of a long metal cylinder in one end of which the charge is heated so that magnesium vapor is formed, which then distils off and is condensed in the cool end. The retort is kept evacuated to a low pressure of a few tenths of a millimeter of mercury. The process has the advantage of requiring lower temperatures than the carbothermic process.

Occurrence of Magnesium

Ores of magnesium are ubiquitous and may depend on one of several different mineral substances for the metal. These include:

$MgCl_2 \cdot 6H_2O$	From sea-water or salt brines
$MgCO_3$	Magnesite
MgO	Periclase
$Mg(OH)_2$	Brucite
$MgCO_3 \cdot CaCO_3$ ·	Dolomite
$MgCl_2 \cdot KCl \cdot 6H_2O$	Carnallite
$MgSO_4 \cdot H_2O$	Kieserite
$MgSO_4 \cdot 7H_2O$	Epsom salts (epsomite)

In all cases comparatively simple chemistry is required to convert the ore to either $MgCl_2 \cdot 6H_2O$ or MgO.

Magnesium as a Metal

Magnesium is an unusual kind of metal. Its various properties do not, in general, parallel those of other structural metals and its behavior is not as predictable. Possibly that is one reason why its indus-

[2] "Some Developments in the Production of Magnesium from Dolomite by the Ferrosilicon Process," by W. M. Pierce, R. K. Waring, C. D. Fetteroff, and G. T. Mahler, *Metals Technology, Technical Publication,* 1707, August, 1944.

trial use has been slow in development. Because of its ready combustibility and the brilliant white light produced when it burns, its earliest use was for flashlights for photography and for pyrotechnic (fireworks) display. For such purposes the magnesium in powder form is mixed with a strong oxidizing agent such as sodium or barium peroxide. When ignited, such a mixture explodes, the heat of reaction illuminating the white MgO to dazzling incandescence.

Experience with these materials has led many to believe that all magnesium is dangerously explosive. This is not true, however, and magnesium in compact form and of moderate section size (½ inch or better) is difficult to ignite. In heavy section ingots, local ignition may be started by a sharp blast flame but will be quenched, upon removal of the flame, by the cooling effect of the adjacent metal.

Workability

The hexagonal close-packed structure of the magnesium crystal space lattice explains some of its fabrication difficulties and behavior in cold working. In cast or annealed form it seems soft enough according to ordinary hardness tests and tensile values to be cold worked readily. Yet, operations like cold rolling, deep drawing, and bending can be performed only under the most carefully controlled conditions and with frequent anneals. Slip in the magnesium crystal takes place at room temperature entirely on the basal plane of the hexagonal lattice, which means that slip directions are few in number compared with those of the face-centered or body-centered cubic metals.

The Ignition Tendency

The casting and heat treating of magnesium and magnesium alloys is complicated by the tendency of the metal to ignite. The situation here is of course different from that of the locally heated cold magnesium noted before. Once ignited, the hot magnesium is difficult to extinguish, water being worse than useless because of the exothermic reaction

$$Mg + H_2O = MgO + H_2.$$
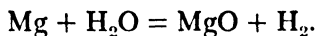
For this reason one of the principal uses for magnesium in warfare is in incendiary bombs.

The volatility of magnesium, coupled with the high fusion temperature of its oxide, helps to explain the ease with which it ignites. Under standard atmospheric pressure (760 millimeters) magnesium boils at 1107°C. At its melting point (651.1°C) it still has a vapor pressure of 2 millimeters of mercury. Its oxide, on the other hand, is one of the

highest melting refractories with a melting temperature in excess of 2800°C. When magnesium burns in air, the oxide forms as a crypto-crystalline (almost amorphous) powder instead of (as in the case of aluminum) a molten oxide to coat and protect the surface from further oxidation.

A comparison of some of the physical constants for magnesium and aluminum is given in Table 1.

TABLE 1.   Physical Constants of Magnesium and Aluminum *

Property	Magnesium	Aluminum
Atomic weight...................	24.32	26.97
Density, g/cm³ at 20°C	1.74	2.70
Coefficient of expansion, 20°C	26.0×10^{-6}	23.86×10^{-6}
Melting point, °C................	651.0	660.2
Boiling point, 760 mm, °C	1107	1800
Vapor pressure, mm Hg..........	2.28 at MP	0.001 at 730°C
Specific heat (0°–100°C)	0.2495	0.2259
Heat of combustion, cal./g.mol.....	146,100	383,900 (Al_2O_3) †
Modulus of elasticity, psi.........	6,200,000	10,300,000

* Values derived mostly from *National Metals Handbook*, 1939, American Society for Metals.

† If the heat of combustion of the Al_2O_3 be divided by 3, the result, 128,000 cal, is the heat per gram atom of oxygen. Values on this basis seem to be fairly indicative of the relative deoxidizing power of most metals. This places magnesium above aluminum in deoxidizing power (where it should be).

Crystallography of Magnesium

The hexagonal close-packed space lattice of magnesium has been noted. The side of the simple hexagon (a_0) is given as 3.2030 A. The height (c_0) of the hexagonal prism is 5.2002 A. The axial ratio (c/a) is 1.6235. The packing of spheres in this arrangement would have an axial ratio of 1.6330, which shows that the magnesium lattice is compressed in the direction of the C axis. A close-packed hexagonal lattice is shown in Figure 28.1. Spheres arranged in the close-packed hexagonal system are shown in Figure 28.2.

The lattice constants for the useful close-packed hexagonal metals are given in Table 2.

With cadmium and zinc the axial ratio is greater than that for spheres, indicating a stretching of the lattice in the direction of the prism axis. Magnesium and cobalt have remarkably similar axial ratios, and beryllium and zirconium are more highly compressed along the C axis than magnesium. It is noteworthy that the ductility and working qualities of these metals are in about the same order as their axial

ratios, beryllium and zirconium being the least ductile and, in fact, brittle, while cadmium and zinc are very ductile and easily workable. Cobalt can be worked although much less easily than iron or nickel.
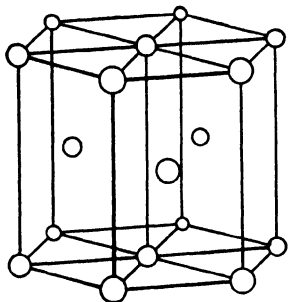
FIGURE 28.1. Close-packed hexagonal space lattice.
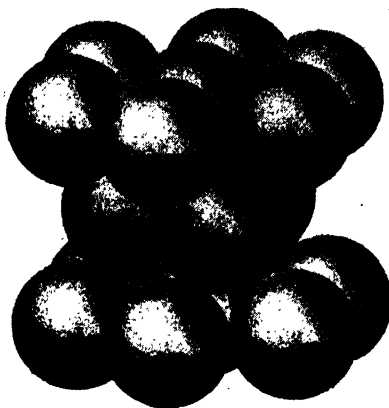
FIGURE 28.2. Arrangement of spheres in close-packed hexagonal system.

TABLE 2. Lattice Constants and Axial Ratios for
Close-Packed Hexagonal Metals

Metal	a_0	c_0	c/a
Be	2.281	3.577	1.568
Cd	2.973	5.606	1.886
Co	2.507	4.072	1.624
Mg	3.2030	5.2002	1.6235
Zn	2.659	4.936	1.857
Zr	3.223	5.123	1.590
Spheres			1.6330

Slip, Twinning, and Plastic Deformation

Recent studies by Barkarian and Mathewson [3] have explained much of the behavior of magnesium toward plastic deformation on the basis of the mechanism of slip and twinning. By careful x-ray analysis they have confirmed much of the earlier work that was somewhat conjectural and have demonstrated these mechanisms with certainty. The

[3] "Slip and Twinning in Magnesium Single Crystals at Elevated Temperatures," by P. W. Barkarian and C. H. Mathewson, *Trans. Am. Inst. Mining Met. Engrs.*, 152 (1943).

black circles of Figure 28.3 represent the bottom layer of atoms in the magnesium unit cell. The open circles represent the next layer above. According to Barkarian and Mathewson, slip is always in the direction
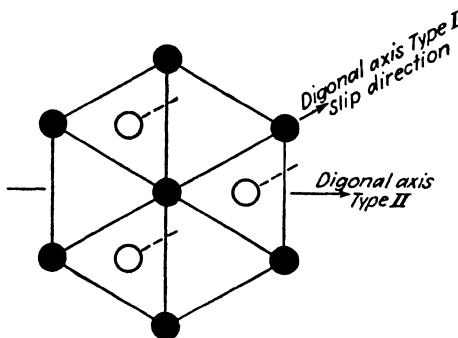
FIGURE 28.3. Projection of the hexagonal close-packed unit cell on the basal plane.

of the *digonal* axis, type I; that is, parallel to the edge of the hexagon. At temperatures below 225°C, the basal plane is the only plane of slip. Thus, slip presumably proceeds by the upper layer of atoms following paths over the lower layer such as are indicated by the dotted lines.

Above 225°C the slipping is not confined to the basal planes; but planes, still parallel to the hexagonal edges and cutting diagonally through the prism, can also act as slip planes. These are illustrated in Figure 28.4. The {101} plane, in addition to the basal plane, can undergo slip at the higher temperature. The {102} plane is a twinning plane, and twinned portions of the magnesium crystal are arranged symmetrically about this plane.

Neither of these planes passes through the intermediate atoms in the prism, and so these atoms would have to be forced out of their relative positions for slip to occur in any direction other than parallel to the edge of the base. Slip on the {101} planes produces crooked and forked slip lines similar to those for alpha iron. However, the possibility, at elevated temperatures, of slip on planes other than the base greatly aids the plasticity of magnesium and permits it to be worked like the cubic metals.

{101} {102} {101}

FIGURE 28.4. Twinning and slip planes in the magnesium lattice at elevated temperatures.

Magnesium Alloys

A survey of the physical properties produced by the addition to magnesium of alloying elements is a little disappointing. The improvements in most cases are mediocre and the properties obtainable in pure magnesium by suitable mechanical treatment rival those of many of the alloys.

Tensile Properties

Magnesium in its purest form, in the cast or annealed condition, is not as soft or as low in tensile strength as either copper or aluminum under like circumstances. On the other hand, magnesium rod of commercial purity in the rolled condition may have a tensile strength of over 35,000 psi [4] with 12% elongation. The maximum tensile strength that is given for magnesium alloys not containing silver in appreciable amount is less than 60,000 psi. With silver up to 5%, a tensile strength of over 65,000 psi has been obtained.

Tensile strengths of between 40,000 psi and 50,000 psi seem to be high values for most magnesium alloys in the heat-treated or rolled condition. Some of these may retain an elongation of 10% or more. It is, of course, an advantage to be able to secure increased strength in castings by heat treatment, and this is effective only in alloys. Also, for high yield strength and high-temperature strength, alloys are essential.

Corrosion

Corrosion resistance is generally lower in magnesium alloys than in pure magnesium. The exception is in alloys with manganese. Manganese is usually incorporated in any magnesium alloy to offset the bad effects on corrosion of the other elements.

Alloying Elements

The principal alloying elements in common use with magnesium are aluminum, manganese, and zinc. In addition, occasional use is made of cadmium, cerium, copper, silicon, silver, and tin. In most of the alloys copper, iron, nickel, and silicon are regarded as impurities. Silicon has considerable importance as an alloying element, however, and copper (because it improves thermal conductivity) has an application in piston alloys.

[4] *Mechanical Properties of Metals and Alloys,* U. S. Bureau of Standards, Circular 447; Book List No. 43, Appendix IV.

Aluminum

Since the real advantage of magnesium as a structural metal is its lightness, it is essential that its alloys retain this lightness as much as possible. Aluminum seems the most logical alloying element to fulfill this requirement, because it too is a structural metal, denser only than magnesium, and (in the quantities used) adding negligible density to the alloy. According to the equilibrium diagram, Figure 27.4, the solid solubility of aluminum in magnesium is 12.1% at the eutectic temperature (438°C) and drops rapidly at lower temperatures. The precipitate phase is the intermetallic compound Al_2Mg_3. This combination of circumstances indicates precipitation hardening characteristics.

However, in keeping with the general behavior of magnesium, the results are not quite up to expectations. Because of the considerable solid solubility at room temperature, only alloys containing more than 7% aluminum are susceptible to age hardening. Even for the alloys that are age hardenable, the results are not spectacular. The values in Table 3 illustrate this.

TABLE 3.   Mechanical Properties of Some Cast
Magnesium-Aluminum Alloys *

Al, %	Mn, %	Form	Tensile strength, psi	Yield strength, psi	Elongation in 2 in., %
4.25	0.20	Cast	24,000	9,000	6
8.0	0.15	Cast, h-t †	33,000	11,000	10
10.0	0.1	Cast	22,000	13,000	2
10.0	0.1	Cast, h-t	35,000	12,000	9
10.0	0.1	Cast, h-t and aged	36,000	19,000	2

* Compiled from Bureau of Standards Circular 447, *Mechanical Properties of Metals and Alloys*, 1943.
† h-t, heat treated by solution treatment only.

Manganese

The solid solubility curve of the magnesium-manganese equilibrium diagram, Figure 28.5, suggests age-hardening characteristics, but such is apparently not the case. There is some disagreement regarding the nature of the precipitate phase. Sawamoto [5] finds the compound Mg_9Mn, while Schmid and Siebel [6] and others believe it to be β manganese.

[5] H. Sawamoto, *Suiyokwai Shi*, 8, 713–727, 763–768 (1935), quoted by Beck, *op. cit.*
[6] E. Schmid and G. Siebel, *Metallwirtschaft*, 1931, quoted by Beck, *op. cit.*

As a matter of fact, manganese has very little effect on the mechanical properties of magnesium and, as noted, its presence is largely for the purpose of improving resistance to corrosion. When present to the extent of 2% or better, it is said to increase the tensile strength
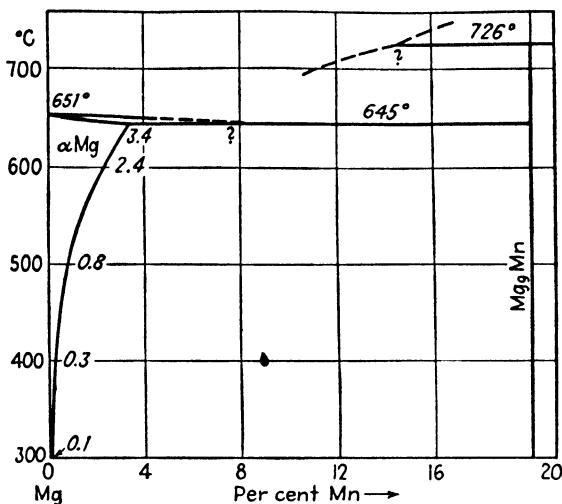
FIGURE 28.5. Partial magnesium-manganese equilibrium diagram according to Schmid and Siebel as quoted by Beck, No. 101 in Book List, Appendix IV.

of wrought alloys. Possibly the fact that the solid solubility drops to a low value by the time the alloy has cooled to 500°C means that not enough manganese is available for precipitation from solid solution at lower temperatures to give hardening or aging effects.

Zinc

On a weight basis, zinc is more effective in hardening and strengthening magnesium than is aluminum. According to the equilibrium diagram, Figure 28.6, the solid solubility of zinc is 8.4% at the eutectic temperature. The precipitate phase corresponds to the formula MgZn, which calls for 72.9% zinc. Below 100°C the solid solubility curve seems to be vertical at about 1.8% zinc. The difficulty of securing true equilibrium in alloys at low temperatures always leaves the lower end of the solvus curve open to question. At any rate the zinc that remains in solid solution has apparently considerable strengthening effect upon the alloy.

Zinc, of course, increases the weight of the alloy and its effect on corrosion resistance is none too good. The combination of aluminum and zinc, on the other hand, is better for corrosion resistance and gives better mechanical properties than aluminum alone.
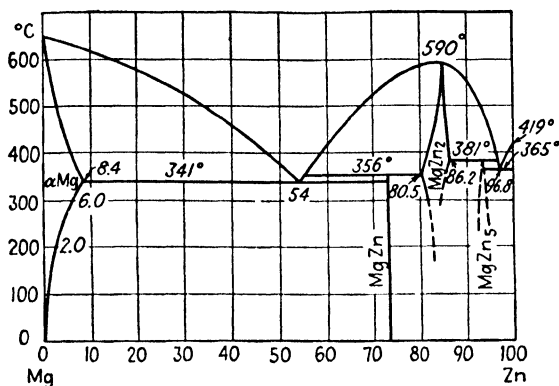
FIGURE 28.6. The magnesium-zinc equilibrium diagram (redrawn from Beck, No. 101 in Book List, Appendix IV).

Other Alloying Elements

Cadmium is used up to 4% in some alloys. Its effect on strength is somewhat less than that of aluminum, but it greatly improves the ductility, particularly toward pressing and forging.

Silver and *cerium* are the greatest strengtheners of magnesium, and with silver especially, alloys are produced having tensile strengths of
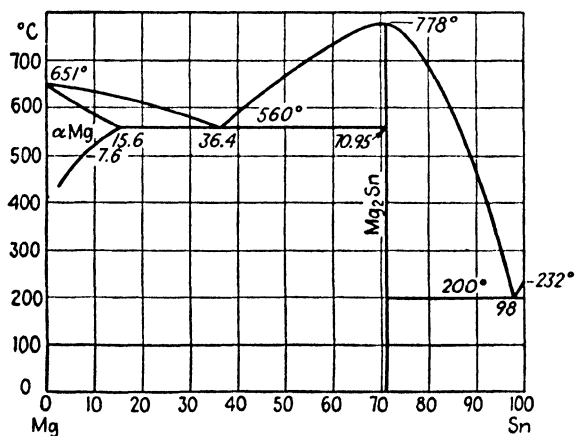
FIGURE 28.7. The magnesium-tin equilibrium diagram (redrawn from Beck, No. 101 in Book List, Appendix IV).

better than 65,000 psi. Silver is used in amounts up to 3% and cerium up to 6% in some commercial alloys. Of course it will be realized that the cost of such alloys would limit them to special purposes.

Silicon is specified in small amount in a number of cast magnesium

alloys. It overcomes hot shortness and helps to overcome cracking due to shrinkage. It is practically insoluble in solid magnesium and adds nothing to the strength.

Tin in the neighborhood of 5% is specified in one forging alloy. Considering the high solid solubility of tin at the eutectic temperature (Figure 28.7), the character of the solvus curve, and the fact that the precipitate phase is the intermetallic compound Mg_2Sn, it is surprising that tin has not found more application in magnesium alloys. It is true that the density of tin is unfavorable, and it is also likely that the current scarcity of tin has prevented its use with magnesium from being exploited. However, in the absence of facts to the contrary, it would appear that tin as an alloy in magnesium should constitute a promising field of exploration.

Metallography of Magnesium and Magnesium Alloys

Because of its reactivity with water, magnesium is somewhat difficult to polish. For final polishing, carefully prepared magnesia powder is usually recommended. This may be suspended in soapy or slightly alkaline water. Earlier stages in the polishing are at the discretion of the operator.

The appearance of the various intermetallic phases and other features of structure are well described by Beck,[7] Woldman,[8] Busk and Anderson,[9] and Peters, Busk, and Elliott.[10] Noteworthy is the observation that the magnesium-magnesium aluminide (Mg_4Al_3) eutectic (Figure 27.4) does not show a characteristic eutectic structure but rather what is described as a divorced eutectic structure. The compound Mg_4Al_3 appears as a more or less continuous network around the magnesium dendrite markings. This structure is not at all unusual in alloys where a solid solution phase is surrounded by a comparatively small amount of the eutectic mixture. It is quite common in white cast irons containing around 2.5% carbon, such as unannealed "malleable." It seems likely that the phenomenon is due to a tendency to form a coarsely dispersed eutectic, coupled with a tendency for the liquid to become supersaturated with respect to the second (nondendritic) phase.

[7] *The Technology of Magnesium and Its Alloys, compiled* by Dr. Ing. E. h. Adolph Beck (translation from the German), F. A. Hughes and Co., Ltd., London. Book List, No. 101; Appendix IV.

[8] "Magnesium," a series of five educational lectures, *American Society for Metals,* Cleveland, Ohio, February, 1946; Book List, No. 94, Appendix IV.

[9] "Water Quenching of Some Typical Magnesium Casting Alloys," by R. S. Busk and R. E. Anderson, *Trans. Am. Inst. Mining Met. Engrs.,* 161: 278 (1945).

[10] "Factors Affecting Abnormal Grain Growth in Magnesium Alloy Casting," by A. T. Peters, R. S. Busk, and H. E. Elliott, *Trans. Am. Inst. Mining Met. Engrs.,* 161: 291 (1945).

Grain Size in Magnesium Alloys

Some unusual phenomena occur in the grain structure and grain size of some magnesium alloys. These phenomena are described and discussed briefly in the following paragraphs.

1. The grain size in cast magnesium-aluminum-zinc alloys can be decreased (refined) by superheating the melt into the neighborhood of 900°C, cooling rapidly to the casting temperature (about 750°C), and casting immediately.[11]

2. The same effect was obtained from temperatures not exceeding 800°C by inoculation with carbon.[10] This was accomplished by stirring pulverized carbon or carbonaceous material into the melt at approximately 750°C, and then raising the temperature to about 800°C.

3. Hultgren and Mitchell [12] find that in some alloys, stirring alone for one minute at 760°C will accomplish the same result. In some alloys, bubbling of acetylene or natural gas through the melt produces grain refinement.

4. In some fine-grained cast alloys, abnormal grain growth occurs on heat treating.[13] This results in occasional very coarse grains in a matrix of fine grains and unpredictable mechanical properties.

5. Beck [14] shows a photomicrograph to illustrate twinning in cast magnesium. This is an unusual phenomenon in cast isomorphous metals.

Magnesium Alloy Specifications

A summary of chemical compositions for magnesium alloys used in the United States is given in Table 4. For the sake of brevity, the data have been abridged and some of the values should be modified for certain applications. In any case the sponsoring organization should be consulted for exact and complete specifications.

Many other compositions are in use for special purposes. If it were not for the cost, silver might possibly be the principal alloying element

[11] "A Study of Factors Influencing Grain Size in Magnesium Alloys," by C. H. Mahoney, A. L. Tarr, and P. E. Le Grand, *Trans. Am. Inst. Mining Met. Engrs.*, 161: 328 (1945).

[12] "Grain Refinement of Magnesium Alloys without Superheating," By Ralph Hultgren and David W. Mitchell, *Trans. Am. Inst. Mining Met. Engrs.*, 161: 323 (1945).

[13] "Factors Affecting Abnormal Grain Growth in Magnesium Alloy Casting," by A. T. Peters, R. S. Busk, and H. E. Elliott, *Trans. Am. Inst. Mining Met. Engrs.*, 161: 291 (1945).

[14] *The Technology of Magnesium and Its Alloys*, compiled by Dr. Ing. E. h. Adolph Beck (translation from the German), F. A. Hughes and Co., Ltd., London. Book List No. 101, Appendix IV.

Table 4. Magnesium Alloys, Specification Numbers and Composition

Specification numbers				Chemical composition, %				Uses†
ASTM *		Dow	Am. Mag.	Al	Mn (min.)	Zn	Others	
Old	New							
11	M1	M	3S		1.20		0.3	S.C., D.C., ingots
11	M1	M	403		1.50		0.3	S.C., D.C., ingots
		L		2.5	0.20		Cd 3.5	Forgings
18	AZ31	FS	52S	2.5– 3.5	0.20	0.7–1.3	0.3	S.C, ingots
15	AZ33	X	74S	2.5– 3.5	0.20	2.5–3.5	0.3	F, extr.
16	AT35		65S	3.0– 4.0	0.2	0.3 max.	Sn 5.0	Forgings
		F	53S	4.0	0.3		0.3	Extr., R.
			244	4.0	0.3		0.3	S.C.
4	AZ63	H	265	5.5– 6.5	0.18	2.7–6.3	0.3	S.C., D.C., ingots
8	AZ61	J	57S	5.8– 7.2	0.15	0.4–1.5	0.3	F, extr., R.
7		E		6.5	0.2			R.
		EX		6.5	0.15		Si 0.1–0.3	D.C.
9	AZ80	O	241	8.0	0.1–1.5	0.2–0.8		S.C., D.C.
13	AZ90	R	58S	7.8– 9.2	0.12	0.5–0.9	0.3	F, R.
17	AZ92	C	263	8.5– 9.5	0.15	1.7–2.3	0.3	D.C., ingots
2	A10	G	260	8.5– 9.5	0.13	0.2	0.3	S.C., D.C., ingots
2	A10	G	240	9.4–10.6	0.13	0.2	0.3	S.C., D.C., ingots
		P	59S	9.4–10.6	0.13	0.7–1.3	0.3	Extr.
14	AZ101	K		9.4–10.6	0.13	0.3 max.	0.3	S.C., D.C., ingots
12	AS100	B	230	9.0–11.0	0.10	0.3 max.	0.3	D.C., ingots
3	A12		246	11.2–12.8	0.10		0.3	S.C., D.C., ingots

* ASTM specification numbers followed by the letter x have narrower specification ranges and lower limits on impurities.
† S.C. = sand castings; D.C. = die castings; F. = forgings; Extr. = extruded bars, rods, and shapes; R. = rolled plate sheet and strip.

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for magnesium. Besides giving increased strength and being especially effective in increasing the yield point, it is very beneficial in magnesium castings. It reduces the tendency to oxidize during melting when present in amounts of less than 1%.

Heat Treatment of Magnesium Alloys

The heat treatment of magnesium alloys parallels that of the aluminum alloys. Solution treatments require lower temperatures than for aluminum alloys and vary with different alloys from 350°C to 425°C. Care must always be taken to prevent excessive oxidation or burning, so the pieces are put in a furnace at about 260°C (Woldman [15]), and brought to the maximum temperature in a period of not less than two hours. The time at temperature is from twelve to twenty hours to effect complete solution in castings.

Rapid air cooling is recommended for solution treatment of castings rather than water quenching. The solution treatment followed by air cooling gives increased strength, ductility, and toughness, but does not greatly increase yield point or hardness. Still greater hardness, higher yield point, and lowered ductility is obtained by aging. For aging treatments, temperatures from 175° to 220°C are recommended and the time is from ten to eighteen hours.

A "stabilizing" treatment consists in heating to 220° to 290°C for two to six hours. This may be applied to the *as cast* or to the solution-treated alloys. In the latter case, it is an aging treatment. It gives complete stress relief and freedom from growth because of aging in service.

Precautions must be taken during heating of magnesium alloys to prevent excessive oxidation or burning. Heating in fused nitrate baths is out of the question, but salt baths containing dichromates have been used. The type of oxidation due to the dichromate apparently forms an impervious protective coating. In furnace heating the atmosphere should be controlled. Above 400°C a concentration of about 1% sulphur dioxide is effective. Below 400°C waste furnace gas or cracked domestic fuel gas containing CO, CH_4, and H_2, is satisfactory.

Working and Forming

Because of the severe work-hardening tendencies, all extensive working and forming operations must be conducted at temperatures above 225°C. Specially heated dies and equipment are used for such purposes. Moderate bending can be performed in the cold if ample

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[15] In "Magnesium," a series of five educational lectures, *American Society for Metals*, Cleveland, Ohio, February, 1941; Book List, No. 94, Appendix IV.

radii are provided. Rolling at temperatures in the neighborhood of 200°C produces materials of maximum strength.

The most satisfactory method of producing magnesium alloy shapes seems to be extrusion. Temperatures in the neighborhood of 400°C are used. The crystal orientation in extruded magnesium is noteworthy.
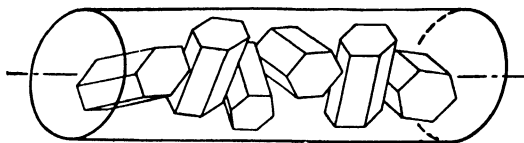
FIGURE 28.8. Crystal orientation in extruded bars (from Beck No. 101 in Book List, Appendix IV).

According to W. Buckmann (in the chapter on "Mechanical Properties," Beck[16]), the crystals align themselves with the prism axis at right angles to the direction of flow, and the digonal axis, type I, in the direction of flow. This gives higher proof stress values in the longitudinal direction.

Melting and Casting

Only brief consideration can be given here to this all-important feature of magnesium technology. Reference is invited to the article on "Magnesium Casting" by Woldman.[17]

Melting is performed in iron or steel crucibles which must be free from nickel. Mixtures of magnesium chloride with sodium or potassium chloride form a fluid flux that is used in the early stages of melting to keep the magnesium cleaned of oxides and nitrides. Later a flux of magnesium chloride and calcium fluoride[18] is sprinkled on top of the melt. This forms a thicker dross which protects the molten metal and absorbs impurities.

Casting presents many problems and is accomplished in numerous ways. Green sand molds can be used but, because of the reactivity of molten magnesium with water, extensive precautions are taken to prevent burning. Oxidation inhibitors in the form of borates, fluorides, and borofluorides are used in the sand and as washes. They are somewhat volatile and also form protective coatings on the metal. Sulphur

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[16] *The Technology of Magnesium and Its Alloys,* compiled by Dr. Ing. E. h. Adolph Beck (translation from the German), F. A. Hughes and Co., Ltd., London. Book List No. 101, Appendix IV.

[17] In "Magnesium," a series of five educational lectures, *American Society for Metals,* Cleveland, Ohio, February, 1941; Book List, No. 94, Appendix IV.

[18] *Magnesium: Its Production and Use,* Ernest V. Pannell, Pitman Publishing Corp., 1944. Book List No. 96, Appendix IV.

dioxide is introduced into the mold, displacing air and moisture. Sulphur dioxide seems to be especially inert toward magnesium.

Permanent molds and die castings are especially adaptable to magnesium. However, special attention must be paid to shrinkage problems and the design must be adaptable to this type of casting.

In all casting the high shrinkage and low strength near the melting temperature are troublesome. Shrinkage is given at 5/32 inch per foot. Ample fillets must be provided and cores must.be soft enough to yield to the pressure of the contracting metal.

In general, the rapid solidification, the low density, and the danger of incorporating the denser dross in the metal, form the basis of many complex problems in casting magnesium.

Corrosion Resistance

The theory of corrosion of magnesium is somewhat too complex for an elementary text. According to Hanawalt, Nelson, and Peloubet,[19] corrosion in salt water is increased by the presence of cathodic particles (separate phases) which set up electrolytic circuits with the magnesium solid solution. However, this effect is greatly reduced by the presence of certain elements in solid solution in the magnesium which affect the potential of the solid solution and also the particle size of the cathodic material. Among the alloying elements, the worst offenders are iron, cobalt, copper, and nickel, while aluminum, manganese, and zinc in themselves do not increase or decrease the corrodibility. However, the bad effects of the first-mentioned metals when present in unavoidable amounts are greatly reduced by small additions of manganese.

Protective Treatments

Magnesium alloys are frequently given protective surface treatments to make them corrosion resistant. There are several such treatments, the most common being dichromate pickle treatments and anodizing treatments. Standardized treatments, as recommended by the American Magnesium Corporation and Dow Chemical Company, are shown in Table 5.

The chrome pickle treatment produces a red and yellow stained surface. There is a small dimension loss of a maximum of 0.0005 inch.

The chrome treatment produces a black or brown coating with practically no dimension change.

[19] "Corrosion Studies of Magnesium and Its Alloys," by J. D. Hanawalt, C. E. Nelson, and I. A. Peloubet, *Trans. Am. Inst. Mining Met. Engrs.*, 147: 273 (1942).

Table 5. Protective Treatments for Magnesium Alloys

Dow	A. M.	Treatment (Woldman, Loose *)
No. 1	A	*Chrome pickle:* 20 seconds to 2 minutes in a bath composed of 180g $Na_2Cr_2O_7 \cdot 2H_2O$ and 187 cc conc. HNO_3 per liter. Hold 5 seconds in air; rinse and dry.
No. 7	G	*Dichromate treatment:* 5 minutes in cold, 15 to 20% HF. Rinse. Then boil 45 minutes in 10 to 15% $Na_2Cr_2O_7 \cdot 2H_2O$.
No. 9	K	*Galvanic anodize:* 5 minutes in 20% HF. Then anodize for 30 minutes at 50 to 60°C in a solution containing 3% each of $Na_2Cr_2O_7 \cdot 2H_2O$ and $(NH_4)_2SO_4$, and 10 cc of NH_4OH (sp. g. 0.88) per liter. Current density: 10 amperes per square foot.
No. 10	L	*Sealed chrome pickle:* Same as *chrome pickle* (No. 1, A) but followed by boiling for 30 minutes in a 10 to 15% solution of $Na_2Cr_2O_7 \cdot 2H_2O$.

* In "Magnesium," a series of five educational lectures, *American Society for Metals*, Cleveland, Ohio, February, 1941; Book List, No. 94, Appendix IV.

The anodizing treatment produces a dark gray to black coating with no dimension change.

The sealed chrome pickle gives the same results as the chrome pickle except that the corrosion resistance is increased due to the sealing of discontinuities or "pores" in the metal.

All the above treatments result in thin layers of mixtures of oxides or hydroxides of magnesium with similar compounds of other elements that are present. These layers adhere tightly to the metal base and act as protective coatings. The coatings may be painted for decoration and also to give additional corrosion protection.

Although the problems involved in magnesium technology are perhaps more numerous and involved than those with other metals, almost all seem to be solvable. Because they tax the ingenuity of the designer, metallurgist, and foundryman, they are really useful in expanding the general field of nonferrous metallurgy, and the future of all metallurgy will be greatly indebted to present day researchers in the metallurgy of magnesium.

QUESTIONS AND PROBLEMS

1. Suggest a reason why aluminum cannot be produced by direct-reduction methods, using carbon, whereas magnesium can be so produced.

2. Show the relation between electrolytic decomposition of H_2O in the electrolysis of $MgCl_2 \cdot H_2O$, and carbon anode consumption.

3. Why should magnesium and barium peroxide explode when ignited together? Calculate the theoretical weight of BaO_2 per pound of magnesium.

4. The heat of formation of MgO is 143,600 calories per gram molecule. That of liquid H_2O is 58,000 calories per gram molecule. What is the heat of reaction of magnesium and water? What other source of heat would ordinarily accompany this reaction?

5. In what way is a close-packed hexagonal lattice for spheres similar to a face-centered cubic lattice, and in what way do they differ?

6. Show that the twinning plane in face-centered cubic metals bisects a layer of close-packed hexagonal cells.

7. Why can strength be increased by heat treatment in magnesium alloys but not in pure magnesium?

8. Explain why manganese, precipitated above 500°C from solid solution in magnesium, might not be expected to give hardening effects.

9. What is meant by a "divorced" eutectic structure? What is an ordinary eutectic structure?

10. Why is it necessary to heat slowly in the solution heat treatment of magnesium alloys?

APPENDIX I

Crystallography of Metal Crystal Lattices

The regular arrangement of atoms described in Chapter II gives rise to layers or *planes* of atoms which pervade the crystal lattice, and in such planes the atomic arrangement also forms a regular geometric pattern. The existence of these planes was assumed in the derivation of Bragg's law and it was explained that several sets of such planes exist in one crystal (Figure 2.7). The spacings of the planes and the atoms in the planes are generally different for each set of planes.

To describe and classify the different sets of planes, crystallographers have devised a system of nomenclature known as the Miller indices. For a full discussion of these, the student is referred to standard texts on crystallography. However, a brief resumé of some of the simpler applications of crystal terminology to the common cubic metal lattices may be helpful in understanding such things as the mechanisms of slip, twinning, and widmanstätten structures.

The first step in the study of crystals is to relate the various planes to a set of coordinate axes. These are chosen so that the planes are grouped symmetrically about each axis and intersect the axes at constant angles. For the six different crystal systems there are six different types of axes. There are usually three axes but in the case of the hexagonal system there are four. The axes intersect at their middle points.

Where all the axes are equal and at right angles, as in the isometric system, the symmetry of the crystal is the same for every direction. Where some of the axes are of different length or inclined, the symmetry is different in different directions. The body-centered and face-centered cubic lattices of most metals belong to the isometric system and consequently are related to three axes of equal length and mutually perpendicular.

If a crystal is placed with its center at the intersection of these axes (i.e., the origin of coordinates) and rotated so that each axis pierces a similar point in the surface of the crystal, the crystal will be symmetrical with respect to its axes and each crystal plane will intersect one or more of the axes in a manner similar to every other plane of the same type. The distances from the origin (O), at which the plane intersects the axes, are called its intercepts. If the longest intercept is called unity, the others are fractions. Thus plane A, shown in Figure I.1, has an intercept of $\frac{1}{2}$ on the X axis, $\frac{1}{2}$ on the Y axis and 1 on the Z axis. Intercepts on the negative ends of the axes are so indicated; e.g., -1, $-\frac{1}{2}$, $-\frac{1}{2}$ are the intercepts for plane B. If any plane of a parallel group is indicated (as when dealing with the space lattices) parentheses are placed around the indices; e.g. (1, $\frac{1}{2}$, $\frac{1}{2}$) means all planes parallel to A.

FIGURE I.1. Coordinate axes for isometric crystals.

The Miller indices use the reciprocals of the intercepts and consequently always have values in whole numbers. If a plane is parallel to any axis its intercept is infinity (∞) and its Miller index is O with respect to that axis. Thus the cube face of Figure I.2 has intercepts 1, ∞, ∞, and Miller indices, 100; in the case of parallel planes (100).

The index of the intercept along the X axis is named first, then that along the Y axis and finally the Z axis. If the intercept is on the negative end of the axis, it is denoted by a minus sign above the index. The indices of all the faces of a cube are:

$$100, \quad \bar{1}00$$
$$010, \quad 0\bar{1}0$$
$$001, \quad 00\bar{1}$$

Since all the faces of a cube are alike and the cube can be turned so that any one of them occupies the 100 position, we may refer to them as a group by placing the characteristic index in braces, thus: {100} means any cube face or plane parallel to it.

In the following diagrams the attempt is made to show the relations between the various planes and the body-centered cubic and face-centered cubic atom arrangements. For simplicity, only the positive

values of the coordinate axes are used; that is, the axes are taken parallel to the edges of the unit cube. In the B diagrams are shown the regular polyhedrons that are formed by the intersection of all planes of a type. The names of these polyhedrons are frequently attached to the types of plane that form them. For instance, a {111} plane is called an octahedral plane; a {110} plane is a dodecahedral plane, etc.
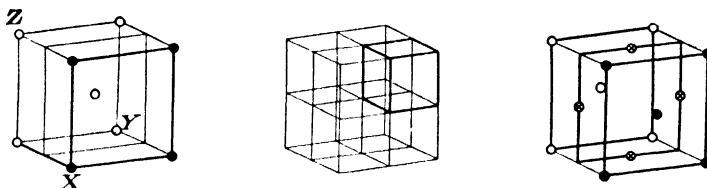
FIGURE I.2. (A) Location of the 100 plane. In body-centered cubes, {100} planes pass through corner atoms or body-center atoms; there is only one grouping of atoms to each plane; cleaving or fracture is frequently parallel to these planes. (B) {100} planes form cubes. (C) In face-centered cubes, {100} planes pass through both corner and face-center atoms. Atoms of both groupings may be in the same plane.
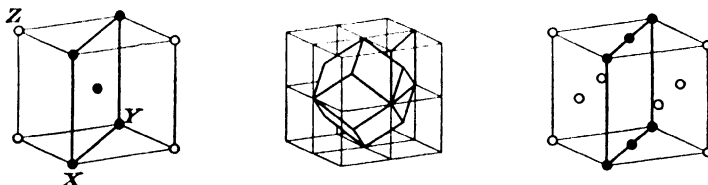
FIGURE I.3. (A) Location of the 110 plane. In body-centered cubes, {110} planes are those of greatest atomic density. They can act as slip planes in this lattice. Precipitation of a face-centered phase occurs parallel to {110} (BCC) planes. (B) {110} planes form dodecahedrons. (C) In face-centered cubes, {110} planes do not have greatest atomic density but contain chains of closest atoms.
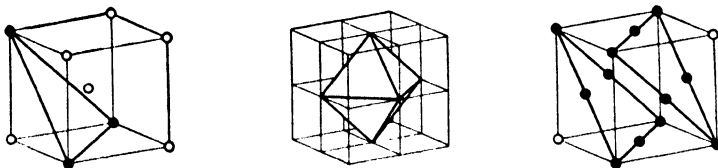
FIGURE I.4. (A) Location of the 111 plane. In body-centered cubes, {111} planes are relatively unimportant. (B) {111} planes form octahedrons. (C) In face-centered cubes, {111} planes are those of greatest atomic density. They are spaced one-third the length of the cube diagonal apart. In this space lattice, {111} planes act as slip and twinning planes. Precipitation of a body-centered phase occurs parallel to {111} (FCC) planes.
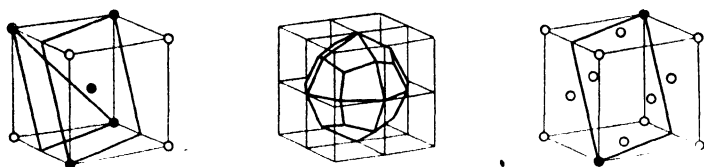
FIGURE I.5. (A) Location of the 211 plane. In body-centered cubes, {211} planes contain chains of closest atoms. They are twinning planes and can act as slip planes. (B) {211} planes form trapezahedrons (tetragonal trisoctahedrons). (C) In face-centered cubes, {211} planes have low atomic density and are unimportant.
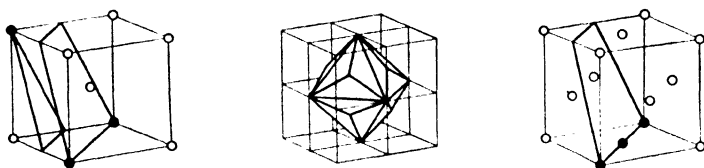
FIGURE I.6. (A) Location of the 221 plane. In body-centered cubes, {221} planes have low atomic density and are unimportant. (B) { 221 } planes form trisoctahedrons (trigonal trisoctahedrons). (C) In face-centered cubes {221} planes contain rather widely separated chains of closest atoms.
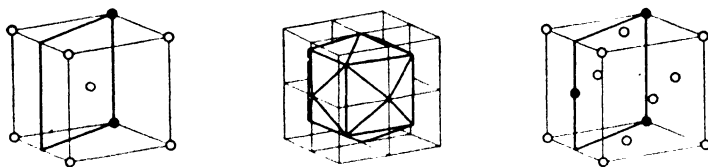
FIGURE I.7. (A) Location of the 210 plane. In body-centered cubes, {210} planes have low atomic density and are unimportant. (B) {210} planes form tetrahexahedrons. (C) In face-centered cubes, {210} planes have low atomic density and are unimportant.
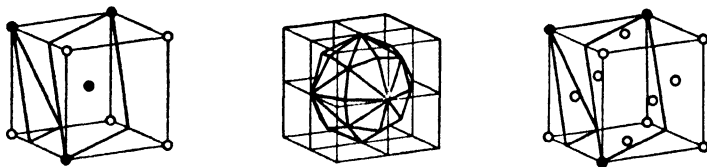
FIGURE I.8. (A) Location of the 321 plane. In body-centered cubes, { 321 } planes contain chains of closest atoms. They occasionally act as slip planes. (B) {321} planes form hexoctahedrons. (C) In face-centered cubes, { 321 } planes have low atomic density and are unimportant.

Directions

In space lattices it is frequently necessary to refer to linear directions. The line representing a direction can be assumed to radiate from the origin, since the origin can always be taken at a point on such a line. The direction of the line is then indicated by the coordinates of a point on the line. The point is so selected that its coordinates are the smallest possible integers. To indicate that they represent direction they are placed in square brackets. Thus the line making equal angles with the X, Y, and Z axis is the [111] direction. It must be remembered that they are not reciprocals as in the case of planes. However, negative values will be obtained, for instance [$\bar{1}$11] is the direction of lines making equal angles with the $-X$, Y, Z axes. All directions of a type are indicated by carets, for instance <111> directions are those making equal angles with any three adjacent axes.

Only in the isometric system are directions perpendicular to planes of the same index. Thus in the body-centered cubes <100> directions are perpendicular to cube faces. Directions <110> are perpendicular to {110} or dodecahedral planes; <111> directions are perpendicular to octahedral planes.

A Derivation of the Phase Rule

Note: This is a modification of the method employed in *Modern Thermodynamics after the Method of Gibbs,* by Guggenheim. It seeks to eliminate the use of thermodynamic terms and to substitute the concept of thermochemical equilibrium as defined in Chapter III. To this end it is necessary to develop the following theorem.

THEOREM: *Phases that are in equilibrium with the same phase are in equilibrium with each other.*

PROOF: By definition, if phase *a* is in equilibrium with phase *b*, phase *a* gives atoms of its various components to *b* at the same rate as it receives, from *b*, atoms of the same components.

If phase *c* is adjusted to be in equilibrium with *b* of the same composition, temperature, and pressure, it must be prepared to lose and receive atoms from *b* in the same manner as does phase *a*.

A moment's reflection should indicate that whatever stands in equilibrium with phase *b* must meet *b*'s conditions of equilibrium because, for equilibrium, *b*'s composition does not change and, therefore, *b*'s gain of each kind of atom will equal its loss of the same kind of atom. Furthermore, this same balance in rate of gain and loss must exist in any domain within *b*'s physical boundaries so that these are the same circumstances as those under which *b* is in equilibrium with itself and are independent of any adjoining material.

Therefore, when phase *c* is in equilibrium with *b*, its atom exchange characteristics are the same as those of *b*, as are also those of phase *a*.

Under these circumstances phases *a* and *c* will, if placed in contact, likewise be in equilibrium.   Q.E.D.

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The Phase Rule

To define completely a system in equilibrium, it is necessary to know the values of the variable quantities.

$$T, \qquad P, \qquad \text{and} \qquad N_i^a, N_k^a, N_i^b, \text{etc.},$$

in which T represents temperature;

P represents pressure; and

N represents by its superscripts and subscripts, the concentration of each component in each phase—that is, N_i^a represents the concentration of component i in phase a.

If there are c components and p phases in a system, there will be pc terms of the type of N_i^a.

With temperature and pressure there will be $pc + 2$ terms describing the system. However, since in each phase the concentrations of the components add up to 1 ($= 100\%$), there will be only $c - 1$ independent concentrations, and hence the number of mutually independent terms will be

$$p(c - 1) + 2. \tag{1}$$

Now with the system in complete equilibrium, each component has distributed itself among the various phases so as to maintain this equilibrium. This distribution is automatic and fixed wth each temperature, pressure, and total amount of each component in the system. The concept of equilibrium states that the rates of reaction in opposite directions are equal so that the rate of loss of a component by any phase is equal to its rate of gain by that phase. Thus the concentration of any component in any phase is such that that phase receives from, and gives to, the system that component at equal rates.

In a system composed of phases $a, b, c, d \cdots$, a is in equilibrium with $b, c, d \cdots$, b is in equilibrium with $a, c, d \cdots$, and so on, so that each phase will be in equilibrium with $p - 1$ other phases. If we write the relationships

a is in equilibrium with b,

b is in equilibrium with c,

c is in equilibrium with d,

etc., and accept the theorem that "phasès that are in equilibrium with the same phase are in equilibrium with each other," no other relationships are needed to describe the system because such equilibrium pairs as a and c follow from the theorem.

In a system of p phases there will be $p - 1$ dependent relation-

ships [1] of this kind *for each component* and hence $c(p-1)$ interdependent concentrations. Thus the number of independent terms necessary to define the system is the total number of terms as computed in (1) minus these interdependent terms:

$$p(c-1) + 2 - c(p-1) = c - p + 2.$$

These terms represent independent variations, i.e., F, of the phase rule, from which

$$F = c - p + 2. \qquad \text{Q.E.D.}$$

[1] This may be likened to a fence where the number of strips of fence (equilibrium relationships) is less by 1 than the number of posts (phases).

Some Schemes for Converting Centigrade to Fahrenheit Temperatures and Vice Versa

The conversion of temperatures from one scale to the other is just a mite too difficult to be performed without the aid of pencil and paper. This, coupled with the fact that in the United States and England there has never been agreement as to which scale should be used, has led to a lot of unnecessary worry and argument. A practice which to the author has seemed deplorable is that employed by some technical societies and publishers in which each temperature in both systems is quoted. "The pieces should be heated to between 1575°F and 1625°F (857°C–885°C) . . . ," takes up unnecessary space, confuses the text, and looks silly. Furthermore, anyone capable of reading the article intelligently should be able to make the conversions to suit his own needs, with a minimum of effort.

The following schemes will help to simplify the problem. The obvious and time-honored methods involve the solution of one of the two equations

$$F = \tfrac{9}{5}C + 32$$

or

$$C = \tfrac{5}{9}(F - 32),$$

where F and C represent the temperatures in Fahrenheit and centigrade degrees, respectively.

For all positive values, Fahrenheit temperatures are numerically greater than centigrade temperatures, so we remember easily to multiply $\tfrac{9}{5}$ when changing from C to F, and by $\tfrac{5}{9}$ when changing from F to C. But it is always necessary to stop and think whether to add or

subtract the 32 and whether to add or subtract it before or after making the multiplication.

If, in either of the equations, we stipulate that $F = C$, the solution is:

$$F = C = -40°$$

Thus, $-40°$ is the temperature at which the Fahrenheit and centigrade values are identical. If we add 40 to either a Fahrenheit or a centigrade temperature, we get its elevation above this common level. Fahrenheit values so obtained are equal to $\frac{9}{5}$ of the centigrade values obtained in the same manner. Thus

$$F + 40 = \tfrac{9}{5}(C + 40),$$

and

$$C + 40 = \tfrac{5}{9}(F + 40).$$

So, to make either conversion, we add 40 to the temperature, multiply the result by $\frac{9}{5}$ or $\frac{5}{9}$ (depending on whether we want our answer in °F or in °C, and subtract 40 from the result. Thus, being given 100°C, and needing to find the Fahrenheit equivalent, we proceed:

$$100 + 40 = 140$$
$$140 \times \tfrac{9}{5} = 252$$
$$252 - 40 = 212°F$$

The multiplication by $\frac{9}{5}$ is a little too tough for most of us to perform in our heads, but try the following:

$$\tfrac{9}{5} = 1.8 = 2.0 - 0.2$$
$$723°C + 40 = 763$$
$$763 \times 2 = \quad 1526.0$$
$$-152.6$$
$$\overline{1373.4}$$
$$-40$$
$$\overline{1333.4°F}$$

Going the other way seems still worse but:

$$\tfrac{5}{9} = 0.5555 \cdots = \tfrac{1}{2} \times 1.1111 \cdots$$
$$2802°F + 40 = 2842$$
$$\tfrac{1}{2} \times 2842 = 1421$$
$$142$$
$$14$$
$$1$$
$$\overline{1578}$$
$$-40$$
$$\overline{1538°C}$$

By carrying out the decimals, the more exact value of 1538.7°C would be obtained.

A little practice in making conversions should fix these methods in the mind of the reader and relieve him thenceforth from concern as to what scale of temperature he is offered.

Finally, one should always remember that temperature *differences* are not concerned with base or zero levels; hence the temperature change in Fahrenheit degrees equals $\frac{9}{5}$ × temperature change in centigrade degrees. That is, a rise of 200°C = a rise of 360°F.

A Selected Book List for Collateral Reading

I. Background and Basic Theory Underlying the Study of Alloy Systems

1. *Atomic Theory for Students of Metallurgy*, by William Hume-Rothery; Institute of Metals Monograph and Report Series No. 3; Institute of Metals, London, 1947. This book is on a graduate level but presented especially for the metallurgist.

2. *Chemistry, A Textbook for Colleges*, by William McPherson, William E. Henderson, Edward Mack, Jr., and W. C. Fernelius; Ginn, 1946. A popular elementary text covering many phases of a very broad subject.

3. "The Hard and Soft States in Metals," by George T. Beilby; *Journal of the Institute of Metals*, London, 1911. This paper is included in this list of book references for its discussion and thought-provoking value. It expands the much discussed hypothesis of the amorphous grain boundary.

4. *Metallurgical Problems*, by Allison Butts; McGraw-Hill, 1943, 2d ed. An excellent text on useful metallurgical calculations. Sufficiently elementary for undergraduate courses.

5. *Mineralogy*, by Edward Henry Kraus, W. F. Hunt, and L. S. Ramsdell; McGraw-Hill, 1936, 3d ed. A complete text on elementary crystallography and mineralogy. Includes a brief chapter on x-ray crystal analysis.

6. *Modern Thermodynamics by the Methods of Willard Gibbs*, by E. A. Guggenheim; Dutton, 1933. This book is included for its exceptionally clear derivation of the phase rule.

7. *The Phase Rule and Its Applications*, by Alexander Findlay, revised by A. N. Campbell; Longmans, 1938. An outstanding and classic treatise on the meaning and use of the phase rule.

8. *Pyrometry*, by William P. Wood and J. M. Cork; McGraw-Hill, 1941. A clear, elementary, college text on temperature measurement.

9. *Structure of Metals*, by C. S. Barrett; McGraw-Hill, 1943. A comprehensive treatise on the crystallography of metals and metal aggregates.

10. *The Structure of Metals and Alloys,* by William Hume-Rothery. The Institute of Metals, London, 1936. A clear and concise exposition of the application of atomic physics to the behavior of metals.

II. Metallography and Physical Metallurgy; General Treatises

11. *Engineering Physical Metallurgy,* by R. H. Heyer; Van Nostrand, 1939. This book contains a large accumulation of material important to a knowledge of physical metallurgy. It has perhaps attempted too much for the space allotted, which makes it difficult to read continuously. It is generously supplied with excellent photomicrographs of both ferrous and nonferrous structures and makes a fine reference book for the student in physical metallurgy.

12. *General Metallography,* by Ralph L. Dowdell and three associates; Wiley, 1943. A comprehensive accumulation of data and illustrations of physical-metallurgical significance. It is well organized and makes an excellent handbook.

13. *An Introduction to the Study of Physical Metallurgy,* by Walter Rosenhain, revised and partly rewritten by J. L. Haughten; Constable (London), 3d ed., 1945. An up-to-date revision of a classic that has retained much of the classicist's viewpoint.

14. *Metals,* volumes I and II, by Sir Harold Carpenter and J. M. Robertson; Oxford University Press, 1939. Probably the most comprehensive of all recent books on physical metallurgy. Volume I is on general principles; volume II covers the special applications to iron-carbon alloys, copper, and other nonferrous alloys.

15. *The Metallography and Heat Treatment of Iron and Steel,* by Albert Sauveur; The University Press, Cambridge, Mass., 3d ed., 1926. This book and the editions that preceded it gave many outstanding American metallurgists their start in metallography. It is beautifully written and illustrated and still worth reading.

16. *Principles of Metallographic Laboratory Practice,* by G. L. Kehl; McGraw-Hill, 1943. A very useful handbook on laboratory technique. Includes material on photomicrography, specimen preparation, and pyrometry.

17. *Principles of Physical Metallurgy,* by Frederick L. Coonan; Harper, 1943. A brief text in metallography with excellent photomicrographs and supplementary drawings.

18. *The Principles of Physical Metallurgy,* by Gilbert E. Doan and Elbert M. Mahla; McGraw-Hill, 2d ed. An excellent nonmathematical text on physical metallurgy.

19. *The Science of Metals,* by Zay Jeffries and Robert S. Archer; McGraw-Hill, 1924. Now very much out of date, but marks an early advance in reasoning on grain growth and the theory of hardening.

20. *Structure and Properties of Alloys,* R. M. Brick and Arthur Phillips; McGraw-Hill, 1942. A short but good text in metallography illustrated with some excellent photomicrographs of ferrous and nonferrous materials.

21. *A Textbook of Metallography*, by Gustav Tammann; translation from 3d German edition by R. S. Dean and L. G. Swenson; Chemical Catalogue, 1925. A classic on physical metallurgy and the interpretation of equilibrium diagrams.

III. Iron and Steel Production Metallurgy

22. *American Malleable Iron;* Malleable Founder's Society, Cleveland, 1944. A complete handbook covering all phases of manufacture and structure of American blackheart malleable. Contains an excellent bibliography and over 100 pages of engineering tables.

23. *Basic Openhearth Steelmaking*, American Institute of Mining and Metallurgical Engineers, Seeley W. Mudd Series, 1944. A comprehensive treatise well illustrated and documented. The first half of the book (Part I) is descriptive of the process; the latter half (Part II) is devoted to the theory and physical chemistry of steelmaking.

24. *The Elements of Ferrous Metallurgy*, by J. L. Rosenholtz and J. F. Oesterle; Wiley, 1938. A book of 252 pages that discusses pig iron, cast iron, wrought iron, and the various steelmaking processes, with chapters on metallography and heat treatment of steels.

25. *Engineering Metallurgy*, by Bradley Stoughton and Allison Butts; McGraw-Hill, 3d ed., 1938. This book covers so wide a field that its treatment of each subject or process is of necessity very brief. It is, however, a ready reference on almost every phase of production and use of ferrous and nonferrous metals.

26. *Ferrous Metallurgy*, volume II, *The Manufacture and Fabrication of Steel*, by Ernest J. Teichert; McGraw-Hill, 1944. The second of a three-volume set of books by the same author. The work is authoritative and up-to-date, with a generous supply of worthwhile data in tables and charts.

27. *Ferrous Production Metallurgy*, by John L. Bray; Wiley, 1942. A well-organized book that brings the subject up to date.

28. *Gray Cast Iron*, by John W. Bolton; Penton, 1937. Some very good photomicrographs of white, gray, and malleable cast iron structures and liberal discussion of properties and equilibrium relationships.

29. *An Introduction to the Metallurgy of Iron and Steel*, by H. M. Boylston; Wiley, 2d ed., 1936. This well-written text constituted an advance in presentation and subject matter over previous publications and, except for the rapidity with which changes were occurring in the industry, should have enjoyed longer popularity than it did.

30. *The Making, Shaping and Treating of Steel*, by J. M. Camp and C. B. Francis; Carnegie-Illinois Steel Corporation, Pittsburgh, 5th ed., 1940. A comprehensive treatise on all phases of steelmaking written for non-metallurgical employees of the U. S. Steel Corporation.

31. *The Metallurgy of Iron and Steel*, by Bradley Stoughton; McGraw-Hill, 1934. For many years was a standard text on iron and steel metallurgy. It still makes a good background for most modern developments.

32. *Modern Metallurgy for Engineers*, by Frank T. Sisco; Pitman, 2d ed., 1948. A well-written and illustrated text of over 450 pages that presents

the physical metallurgy and application of ferrous and nonferrous alloys in a manner understandable to all engineers.

33. *Wrought Iron,* by James Aston and Edward B. Story; A. M. Byers Co., Pittsburgh, Pa., 3d ed., 1939. A well-written description of the chemistry, structure, and production of wrought iron by old and new methods.

IV. Heat Treatment and Properties of Commercial Steels

34. *Alloy Constructional Steels,* by Herbert J. French. American Society for Metals, Cleveland, 1942. A practical reference book that describes and defines the tests and terms applied to alloy steels. Well illustrated and quite comprehensive for a book of only 267 pages.

35. *The Alloys of Iron and Carbon,* volume I, *Constitution,* by Samuel Epstein; McGraw-Hill, 1936, Alloys of Iron Research Monograph Series. An authoritative work covering the metallography and principles of heat treatment and behavior of all iron-carbon alloys.

36. *The Alloys of Iron and Carbon,* volume II, *Properties,* by Frank T. Sisco; McGraw-Hill, 1937, Alloys of Iron Research Monograph Series. Deals with physical and mechanical properties and tests, creep tests, corrosion, magnetic and electric properties, and other phases of iron-carbon alloys.

37. *Atlas of Isothermal Transformation Diagrams;* United States Steel Corporation of Delaware, Pittsburgh, Pa., 1943. A loose-leaf collection of 56 S curves with an introductory comment and explanation. Contains a very good selected bibliography.

38. *Bethlehem Alloy Steels;* The Bethlehem Steel Co., Bethlehem, Pa., 1935. A useful compilation of data on standard steels. Includes considerable descriptive matter, also physical-property charts and grain-size charts. Noteworthy are a color chart to show incandescent colors and a color chart to show temper colors.

39. *Carbon and Alloy Steels, Properties;* booklet 211, Bethlehem Steel Co., Bethlehem, Pa., 1946. A revision and sequel to earlier publications, such as *Bethlehem Alloy Steels.* Lists AISI steels and discusses hardenability, induction hardening, and other new tests and treatments.

40. *Cast Metals Handbook,* American Foundrymen's Association, Chicago, 3d ed., 1944. A standard handbook on the properties of cast steel, cast iron, malleable iron and cast nonferrous alloys.

41. *Engineering Materials and Processes,* by William Howard Clapp and Donald Sherman Clark; International, 1938. An elementary text descriptive of many processes of manufacture and fabrication of metals and plastics. Principal emphasis is on ferrous metals. Profusely illustrated with excellent drawings and halftones.

42. *Heat Treatment of Soft and Medium Steels,* by Federico Giolitti, translated by E. E. Thum and D. G. Vernaci; McGraw-Hill, 1921. This old-timer is recommended for the clear analytical thinking that is displayed in it.

43. *Mechanical Properties of Metals and Alloys,* by John L. Everhart, Earl W. Lindlief, James Kanegis, Pearl G. Weissler, and Frieda Siegel; National Bureau of Standards Circular C447, U. S. Government Print-

ing Office, Washington, D. C., 1943. One of the most comprehensive lists of alloys and properties available.

44. *The Metallurgy of Steel Castings*, by Charles Willers Briggs; McGraw-Hill, 1946. Manufacture, metallography, and heat treatment of steel castings. Some excellent photomicrographs of cast structures.

45. *Metals and Alloys Data Book*, by S. L. Hoyt; Reinhold, 1943. A fine compilation of useful data on properties of ferrous and nonferrous alloys.

46. *National Emergency Steels;* American Society for Metals, 2d revision, 1943. A pamphlet of 72 pages devoted to the description, properties, and purposes of the National Emergency Steels.

47. *National Metals Handbook;* American Society for Metals, 1948. The outstanding handbook on properties, uses, treatment, and physical metallurgy of metals and industrial alloys.

48. *S.A.E. Handbook;* Society of Automotive Engineers; issued annually. A standard work on S.A.E. steels; gives specifications and recommended treatments and compositions.

49. *Steel and Its Heat Treatment*, volume I, *Principles, Processes, and Control,* by D. K. Bullens and Battelle Memorial Institute; Wiley, 1947. A handbook and reference book for the steel treater.

50. *Steel and Its Heat Treatment*, volume II, *Engineering and Special Purpose Steels,* by D. K. Bullens and Battelle Memorial Institute; Wiley, 5th ed., 1947. A handbook and reference book for the steel treater. This and volume I constitute the most up-to-date and comprehensive treatise available on the heat-treatment of steels.

51. *U.S.S. Carilloy Steels;* Carnegie-Illinois Steel Corp., Pittsburgh, 1938. Classified information on the treatment and properties of a variety of alloy steels. Chapters on S curve, hardenability, grain size, and other factors. Pleasingly written and beautifully illustrated.

V. Mechanical Testing

52. *Creep.* The best data on creep will be found in *Transactions of the American Society for Metals, Transactions of the American Institute of Mining and Metallurgical Engineers,* and *Proceedings of the American Society for Testing Materials,* during the years 1940 to 1948.

53. *Creep Data;* American Society of Mechanical Engineers and American Society for Testing Materials Research Committee; published jointly by the two Societies, 1938. A compilation of over 800 data sheets for creep tests on carbon and alloy steels and nonferrous alloys. The material is well arranged and includes comparative tensile, hardness, and impact tests, but the book refrains from advancing any theory or attempt at correlation of creep with other properties.

54. *Creep of Metals,* by H. J. Tapsell, Oxford University Press, 1931. A standard work describing methods and principles. Obviously somewhat out of date.

55. *The Fatigue of Metals,* by H. F. Moore and J. B. Kommers; McGraw-Hill, 1927. This is a standard work on methods and results of fatigue testing.

56. *The Hardenability of Alloy Steels;* American Society for Metals, 1939. Symposium on the hardenability of alloy steels. Nine papers with discussions.

57. *Hardness and Hardness Measurements,* by Samuel R. Williams; American Society for Metals, Cleveland, 1942. A comprehensive discussion of all hardness tests to date of publication, written in an easy style and profusely illustrated.

58. *The Hardness of Metals and Its Measurement,* by Hugh O'Neil; Chapman and Hall, 1934. The first thoroughgoing treatise on hardness testing. Presents critical discussions of the advantages and limitations of each method.

59. *Materials of Construction,* by J. B. Johnson, rewritten by M. O. Withey and James Aston; Wiley, 8th ed., 1939. A classic and standard treatise on the properties and methods of testing of engineering materials. Covers both metallic and nonmetallic materials.

60. *Prevention of Failure of Metals under Repeated Stress,* Battelle Memorial Institute; Wiley, 1941. A clearly written and simple discussion of the general subject of fatigue of metals. Profusely illustrated.

61. *Symposium on Impact Testing;* American Society for Testing Materials, 1938. An authorized reprint of articles published in the *Proceedings* of the Society. Nine papers by various authorities and an introduction by M. F. Sayre and Walter W. Waring.

62. *Symposium on the Significance of the Hardness Test of Metals in Relation to Design;* American Society for Testing Materials, 1943. Three papers on principles and comparative results; general discussion and tentative hardness conversion tables.

63. *Symposium on the Significance of the Tension Test of Metals in Relation to Design;* 4 papers and discussions; American Society for Testing Materials, reprint, 1940. These papers are interesting and enlightening but on an advanced graduate level.

VI. Carburizing, Nitriding, and Furnace Atmospheres

64. *Carburizing (Symposium);* American Society for Metals, 1938. The papers and discussions constituting the symposium on carburizing at the annual meeting in 1937.

65. *Case Hardening of Nickel Alloy Steels,* Section VI, Data Sheet No. 5, *Nickel Alloy Steels;* International Nickel Co., Inc., New York, 1941. A terse but pithy discussion of pack, gas, and liquid-bath carburizing, and heat treatment of the carburized pieces.

66. *The Cementation of Iron and Steel,* by Federico Giolitti, translated by Joseph W. Richards and Charles A. Rouiller; McGraw-Hill, 1915. This classic is well worth reading for the history of the research and development of carburizing that it contains. It marks the change in carburizing from an ancient art to a modern industrial process with a scientific background.

67. *Industrial Controlled Atmospheres,* by Norbert K. Koebel; Lindberg Engineering Co., Chicago, 1942. A brief but clear presentation of the problem of controlled atmospheres, well illustrated.

68. *Industrial and Electric Heating,* by Numan R. Stansel; Wiley, 1933. This book deals with furnaces mostly from a metallurgical and heat-treatment standpoint. Chapter VIII contains an excellent discussion of furnace atmospheres.

69. *Nitriding Symposium;* American Society for Steel Treating, 1929. A collection of eight papers and discussions reprinted from the *Transactions* of the Society.

VII.   Alloy Steels

70. *The Alloys of Iron and Nickel,* volume I, *Special Purpose Alloys,* by J. S. Marsh; McGraw-Hill, 1938. A thoroughgoing treatise on the various properties, including thermal, magnetic and mechanical properties, of iron-nickel alloys. Contains a bibliography of over 600 references, arranged in order of date of publication.

71. *Alloys of Iron and Chromium,* volume I, *Low-Chromium Alloys,* by A. B. Kinzel and Walter Crafts; McGraw-Hill, 1937. Alloys of Iron Monograph series, The Engineering Foundation. This and volume II constitute a comprehensive treatise on all phases of iron-chromium alloys. Volume I deals principally with the constructional steels containing less than 5% Cr, but includes an extensive discussion of the metallography of the iron-chromium-carbon system. Bibliography of 478 references.

72. *Alloys of Iron and Chromium,* volume II, *High-Chromium Alloys,* by A. B. Kinzel and Russell Franks; McGraw-Hill, 1940. Alloys of Iron Monograph series, The Engineering Foundation. This second volume of the iron-chromium series completes the compilation of available data on these alloys: It deals with all phases of stainless steels and high-chromium cast irons. Bibliography of 528 references.

73. *The Alloys of Iron and Molybdenum,* by J. L. Gregg; McGraw-Hill, 1932; Alloys of Iron Monograph series, The Engineering Foundation. A summary of available data on all phases of molybdenum steels, including molybdenum high-speed steels and molybdenum nitriding steels.

74. *Functions of the Alloying Elements in Steel,* by E. C. Bain; American Society for Metals, 1939. A clear exposition of the story of alloy steels, written in an easy style and beautifully illustrated.

75. *High-Speed Steel,* by Marcus A. Grossmann and Edgar C. Bain; Wiley, 1931. A useful reference book on the manufacture, treatment, and uses of tungsten high-speed steel. Very little on molybdenum, and the book is somewhat out of date.

76. *Molybdenum,* by R. S. Archer, J. Z. Briggs, and C. M. Loeb, Jr.; Climax Molybdenum Co., New York, 1948. A complete and up-to-date treatise on molybdenum steels, irons, and other alloys. Contains many original diagrams and S curves. Heavily documented.

77. *Molybdenum in Steel;* Climax Molybdenum Co., New York, 1939–1942. Thirteen loose-leaf sections in a handbook on the properties and uses of molybdenum steels. Contains some excellent and original S curves.

78. *Molybdenum Steels,* by Julius L. F. Vogel and W. F. Rowden; High Speed Steel Alloys, Ltd., Widnes, England, 1935. A brief but pithy description of methods of manufacture, types, and properties of some principal types of molybdenum steel as applied in England.

79. *Nickel Alloy Steels;* International Nickel Co., New York, 1934–1939. Loose-leaf handbook with important data and charts on the principal nickel steels and high nickel ferrous alloys.

80. *Properties of Frequently Used Carbon and Alloy Steels;* booklet 211, Bethlehem Steel Company, Bethlehem, Pa., 1946. A useful compilation of data on standard steels.

81. *Republic Alloy Steels;* Republic Steel Corporation, Cleveland, 1938. A well-organized handbook with ample descriptive matter. Contains physical-property charts and specifications for about 30 S.A.E. steels; also grain-size charts. Noteworthy is an interesting chapter on the McQuaid-Ehn test.

82. *Stainless Irons and Steels,* by J. H. G. Monypenny; Wiley, 2d ed., 1931. A standard British treatise on all phases of stainless steels.

83. *Stainless Steels,* by Percy H. Miller; Oxford University Press, 1937. A pocket-size instruction book in the selection and use of stainless steels and other stainless alloys, notably inconel. Written in England.

84. *Tool Steels,* by J. P. Gill and four associates; American Society for Metals, 1934.

VIII. Nonferrous Alloys

85. *ALCOA Aluminum and Its Alloys;* Aluminum Company of America, Pittsburgh, 1946, 1947. The most inclusive of several booklets published at frequent intervals by the Aluminum Company. This one gives properties, specifications, and uses of the cast and wrought alloys.

86. *Annotated Equilibrium Diagrams, Series No. 3,* by G. V. Raynor; Institute of Metals, London, 1944. Equilibrium diagrams of all the binary systems brought up to date with notations and complete bibliographies.

87. *Arsenical and Argentiferous Copper,* by J. L. Gregg, Chemical Catalogue, 1934. A gem of a book of 175 pages that discusses the history, properties, and uses of copper and presents valuable data and tables on arsenical and argentiferous copper.

88. *Der Aufbau der Zweistofflegierungen,* by M. Hansen; Julius Springer, Berlin, 1936; photolithoprint reproduction by Edwards Brothers, Inc., Ann Arbor, Michigan. A compilation with discussions, 1943, of all available binary equilibrium diagrams to date of publication. Knowledge of German is not necessary for use of the equilibrium diagrams.

89. *Cold Working of Brass, with Special Reference to Cartridge Brass,* by L. E. Gibbs; American Society for Metals, 1946. A 100-page booklet that is jammed with useful information, excellent photomicrographs and grain-size charts.

90. *Copper and Copper Base Alloys,* by R. A. Wilkins and E. S. Bunn; McGraw-Hill, 1943. A systematic compilation of descriptions, physical-property tables, and mechanical-property charts for the various commercial forms of copper and copper alloys.

91. *Effect of Impurities in Copper*, by S. L. Archbutt and W. E. Prytherch; British Nonferrous Metals Research Association, London, 1937. A standard British work that compiles much of the information available at time of publication. Discusses the effects of most other elements on the electrical and mechanical properties.

92. *The Heat Treatment and Annealing of Aluminum and Its Alloys*, by N. F. Budgen; Sherwood Press, Cleveland, 1933. A standard treatise on all phases of aluminum technology, somewhat out of date.

93. *Impurities in Metals*, by Colin J. Smithells; Wiley, 2d ed., 1931. Now quite out of date but contains valuable information regarding the effects of minor constituents and trace elements.

94. *Magnesium. A series of Educational Lectures by five authorities;* American Society for Metals, 1946. Titles of papers are: Extractive Metallurgy; Structural Design; Castings; Wrought Alloys; and Corrosion and Protection.

95. *Magnesium and Its Alloys*, by J. L. Haughten and W. E. Prytherch, Chemical Publishing Co., 1938. A short summary of available information with data on melting, working, and the metallography of magnesium and magnesium alloys. Supplemented with an extensive list of equilibrium diagrams.

96. *Magnesium, Its Production and Use*, by Ernest V. Pannell; Pitman, 1944. A condensed discussion of the properties, methods of production, and use of magnesium and magnesium alloys.

97. *Metallography of Aluminum Alloys*, by Lucio F. Mondolfo; Wiley, 1943. Part I presents in alphabetical order the equilibrium diagrams of aluminum with other elements. It includes some ternary and quaternary systems. The rest of the book deals with the metallography and treatment of commercial alloys. Probably the best collection of photomicrographs available; over 1000 references.

98. *Metallurgy of Copper*, by Joseph Newton and Curtis L. Wilson; Wiley, 1942. A complete and useful text that describes the chemistry and metallurgy of copper smelting by many methods and contains much useful data on alloys and commercial production of copper.

99. *The Playbook of Metals*, by John Henry Pepper; Routledge, Warne and Routledge, London, 1861. A quaint book of the past; contains interesting discussions of each of the metals then known with authoritative historical sketches. Considerable space given to English coal-mining methods. Illustrated with nearly 300 engravings.

100. *Symposium on Stress-Corrosion Cracking of Metals;* American Society for Testing Materials, and American Institute of Mining and Metallurgical Engineers, 1944. A collection of 30 papers and discussions. A complete and authoritative treatise.

101. *The Technology of Magnesium and Its Alloys*, compiled by Dr. Ing. E. h. Adolph Beck; translation from the German by F. A. Hughes and Co., Ltd., 3d ed., London, 1943. A collection of articles by several writers. Deals with all phases of magnesium including methods of production, physical metallurgy, and applications. Probably the most authoritative and comprehensive work at the time of its production.

Books Recommended as Collateral Reading in Connection with Each Chapter

Obviously, many of the books in the list of Appendix IV carry information that applies to more of the text than is indicated in the following table. Furthermore the selection here offered is not the only one, possibly not the best one, that might be made. However, the student will find in the present allotment, as has the author, material that should stimulate his interest and enhance his understanding of the subject matter of the text.

The books selected are written in English, with the exception of No. 88, and are available in most engineering libraries. A knowledge of German is not necessary for the utilization of the equilibrium diagrams in reference 88.

Allotment of Books by Chapters

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XXVII	5, 19, 20, 47, 85, 86, 88,° 92, 97, 99
XXVIII	5, 9, 43, 47, 86, 88,° 94, 95, 96, 101

° In German. The equilibrium diagrams may be used without a knowledge of German.

The Use of Periodical Literature in Teaching Physical Metallurgy

Shortly after his introduction to physical metallurgy, the student is confronted with the necessity for keeping up with new developments. This will probably be true for a long time to come because, by its very nature, the subject is continually developing and expanding, and no textbook can be completely up to date. Nor, indeed, should it try to be; rather should it seek to acquaint the student with those principles and techniques that will enable him to comprehend the new developments as they are brought forth in current periodical literature.

A common teaching practice, used by the present author, is to assign to each student an article of current interest to be read and abstracted, its subject matter to be presented orally to the class. This may be followed by a short discussion by the class as a whole. It is felt that this procedure bears fruit later, when the student is called upon to present his own thesis or dissertation.

The periodicals in which such assignments are made are those that are easily available in an engineering library and are published in English. It is felt that articles dealing with research projects are more valuable for this purpose than descriptive or popular articles. The following list of well-known periodicals should serve as a guide in making such assignments.

I. **Periodicals Devoted to Reporting New Developments and the Results of Research**

1. The American Foundrymen's Association, Chicago. *Transactions*, published quarterly.

2.*American Institute of Mining and Metallurgical Engineers, New York.
   (a) *Transactions, Institute of Metals Division,* published annually.
   (b) *Transactions, Iron and Steel Division,* published annually.
   (c) *Metals Technology,* published eight times a year (mostly preprints of the articles in both *Transactions*).
3. American Society for Metals, Cleveland. *Transactions,* two volumes published annually. Preprints of papers available to members on request.
4. American Society for Testing Materials, Philadelphia.
   (a) *Proceedings,* published annually.
   (b) *Standards,* published every three years with annual supplements.
5. Institute of Metals (Great Britain), London. *The Journal,* published annually.
6. Iron and Steel Institute (Great Britain), London. *The Journal,* two volumes annually until 1947, published monthly since 1947.
7. *Science Reports,* Tôhoku Imperial University, Japan. Last volume received March, 1941.

II.   Periodicals Containing Descriptive and Semitechnical Articles

1. *Foundry,* Penton Publishing Co., Cleveland, published monthly.
2. *Iron Age,* Chilton Co., New York, published weekly.
3. *Iron and Coal Trades Review,* London, published weekly.
4. *Light Metal Age,* Chicago, published bimonthly.
5. *Materials and Methods,* Reinhold Publishing Corp., New York, published monthly.
6. *Metallurgia (The British Journal of Metals),* Kennedy Press, Manchester, England, published monthly.
7. *Metal Progress,* American Society for Metals, Cleveland, published monthly.
8. *Mining and Metallurgy,* American Institute of Mining and Metallurgical Engineers, New York, published monthly.
9. *Steel, The Magazine of Metal Working and Metal Producing,* Penton Building, Cleveland. Strictly a trade journal, published weekly.

III.   Abstracts and Lists of Articles

1. *Bulletin,* Iron and Steel Institute (British), London. Published monthly and reprinted in the *Journal.*
2. *Chemical Abstracts,* American Chemical Society, Easton, Pa., published monthly.
3. *Metallurgical Abstracts,* Institute of Metals (British), London, published annually.
4. *Metals Review,* American Society for Metals, Cleveland, published monthly, compiled in book form annually.
5. *Mining and Metallurgy,* American Institute of Mining and Metallurgical Engineers, New York, published monthly.

* Starting in 1949 the metallurgical publications of AIME are to be combined in the *Journal of Metals,* published monthly.

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